NEW CONCEPTIONS IN COLLOIDAL CHEMISTRY

BY THE SAME AUTHOR

THE ELEMENTS OF COLLOIDAL CHEMISTRY
COLLOID AND CAPILLARY CHEMISTRY

NEW CONCEPTIONS IN COLLOIDAL CHEMISTRY

BY

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WITH 47 DIAGRAMS AND 20 TABLES

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PREFACE

SCIENCE consists in approximations. We first form a more or less rough and crude picture of the phenomena we are dealing with and then draw it more exactly and with greater precision, as our knowledge grows. This development may be observed very clearly in capillary and colloidal chemistry. The general conceptions of adsorption, the electric potential of surfaces, the state of aggregation and the shape of colloidal particles, which conceptions were sufficient some years ago, had to be worked out in greater detail in order to account for manifold new experimental results. The following chapters contain some examples of this development. They may be useful to those who wish to look back on the growth of science, as well as to those who hope to find new suggestions.

This little book contains the subject-matter of lectures delivered in the United States during the summer of 1925, and mostly written in their present form during a prolonged stay at the

University of Minnesota, Minneapolis. In preparing the English text I received a very large measure of help from Professor L. H. Reyerson, to whom I desire once more to tender my heartiest thanks. I am also greatly indebted to Professor G. Barger of Edinburgh for various suggestions and for reading the proofs.

H. FREUNDLICH

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CHAPTER I

ADSORPTION

ADSORPTION is regarded as a loose chemical union or as a surface phenomenon, ruled by Gibbs' equation which correlates adsorption with surface tension. Neither conception implies any special assumption concerning the shape of the molecules adsorbed or their orientation on the surface. Now these general conceptions have not proved sufficient to explain that very general and important rule which is known as Traube's rule. E. Duclaux [1] and especially I. Traube [2] showed that capillary-active organic substances such as alcohols, aldehydes, ketones, fatty acids, amines, and other organic non-electrolytes or weak electrolytes lower the surface tension to a greater degree as the length of the carbon chain increases in the homologous series. In Fig. 1, p. 2, the abscissæ are concentrations c, in moles per liter, and the ordinates the surface tension σ, in dynes per centimeter. This regular change in surface tension can be

expressed quantitatively if the formula of Szyszkowski [3] is used. In this formula

$$\Delta = \frac{\sigma_M - \sigma_L}{\sigma_L} = b \log\left(\frac{c}{k} + 1\right).$$

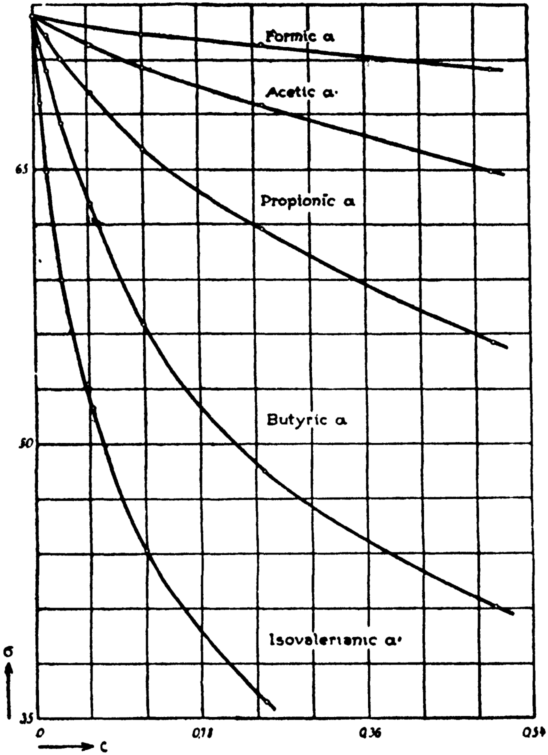

FIG. 1.

σ_M is the surface tension of water, σ_L the surface tension of the solution, and b and k are constants. b is practically the same for all substances. k is a constant

which is characteristic of each substance. It is the concentration for which the relative lowering of the surface tension Δ has a value of 0·1387. k is therefore the measure of the capillary activity of these organic substances. As the capillary activity of the substance increases the value of k becomes smaller. In order to have a measure of capillary activity, which increases with Δ, the reciprocal value of k, $o = \frac{1}{k}$ is often used. This value is called the specific capillary activity. The following table shows the change of o for a series of fatty acids :—

TABLE 1 [4]

Substance.	b.	k.	o.	$\frac{o_{n+1}}{o_n}$.
Formic acid	(0·1252)	1·38	0·73	—
Acetic acid	0·1252	0·352	2·84	3·9
Propionic acid	0·1319	0·112	8·93	3·1
n-Butyric acid	0·1792	0·051	19·6	2·2
n-Valeric acid	0·1792	0·0146	68·5	3·5
n-Hexoic acid	0·1792	0·0043	233	3·4
n-Heptoic acid	0·2575	0·0018	555	2·4
n-Octoic acid	0·2489	0·00045	2220	4·0
n-Nonoic acid	(0·2389)	0·000014	7140	3·2

o increases in a geometrical series whereas the molecular weight of the acids increases in an arithmetical series. Traube's rule may therefore be expressed by the formula,

$$o = e^{\kappa M} \quad . \quad . \quad . \quad . \quad (1)$$

where M is in the molecular weight of the fatty acid and κ is a constant. If we compare two successive members of a homologous series we have the formula,

$$\frac{o_{n+1}}{o_n} = e^{\kappa(M_{n+1} - M_n)}. \qquad (2)$$

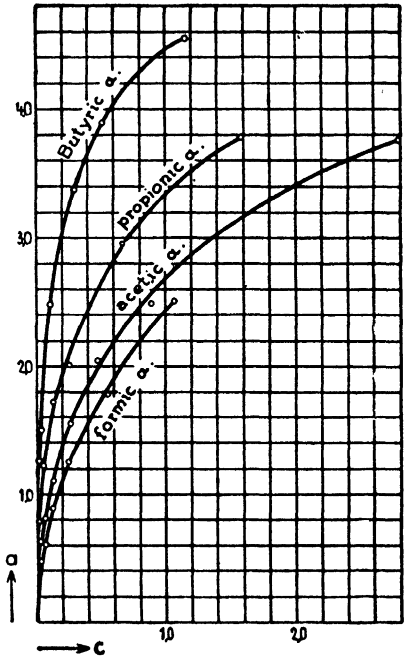

FIG. 2.

A similar rule holds for the adsorption of these organic substances on adsorbents such as charcoal in aqueous solutions. (In Fig. 2, the abscissæ c are equilibrium concentrations in moles per liter, the ordinates a, adsorbed amounts in millimoles per gram of

charcoal.) According to the Gibbs' adsorption formula, the amount adsorbed is related to the lowering of the surface tension. We therefore find a large increase in the amounts adsorbed as we ascend the homologous series.

As I mentioned before, the usual assumptions concerning adsorption do not give any explanation for Traube's rule. Langmuir [5] succeeded in accounting for the phenomena in the following manner. It may be shown that, as a first approximation, σ is proportional to $\frac{a}{c}$, i.e. the ratio of the amount adsorbed, a to the equilibrium concentration c. Now for $\frac{a}{c}$ Boltzmann's formula gives,

$$\frac{a}{c} = \mathrm{K}e^{\frac{\lambda}{\mathrm{RT}}} \quad . \quad . \quad . \quad (3)$$

K is the constant and λ is the energy necessary to transfer one mole of the capillary-active substance from the surface to the interior of the solution. Since $\frac{a}{c}$ is proportional to σ, equation (3) also holds for σ (with a new constant K′) and so, combining equation (3) and (1) and comparing two substances as in equation (2), the following expression may be derived :—

$$\lambda_{n+1} - \lambda_n = \kappa \mathrm{RT}(\mathrm{M}_{n+1} - \mathrm{M}_n) \quad . \quad . \quad (4)$$

This means that the energy necessary to transfer one mole of the capillary-active substance from the surface to the interior of the solution increases by a definite value, which is the same for each addition of a CH_2

group. This can only be understood if each new CH_2 group has the same influence on this energy as any other CH_2 group. The molecules of the capillary-active substances must therefore lie flat on the surface of the solution in order to explain Traube's rule. Furthermore, the energy necessary to transfer the molecules into the interior of the liquid is not influenced by any specific attraction which might exist between the adsorbent and these organic molecules.

In order to explain Traube's rule, a special orientation of molecules on the surface must be assumed. On the other hand, the surface of many adsorbents cannot be regarded as being absolutely homogeneous. Any single unit of the surface is not exactly like any other unit of surface, but it must be assumed that the surface has a certain structure. O. Warburg [6] showed that the behaviour of blood charcoal could only be explained from this point of view. As a result of these assumptions, he was able to synthesize a charcoal having the same properties as blood charcoal.

Blood charcoal catalyses the oxidation of amino-acids, such as cystine, leucine and others, by oxygen in aqueous solution. The reaction proceeds on the surface of the charcoal. This can be proved because the addition of capillary-active substances retards the reaction and this retarding effect increases with the amount of surface covered by the capillary-active substance. In the following table a comparison is made between the amounts of capillary-active substances which retard the oxidation of cystine in the presence of blood charcoal to the same degree, and those amounts

are equal which caused a given displacement of the cystine from the surface. They all lower the amount of cystine, adsorbed from a pure solution, from 0·05 millimols of cystine per gram of charcoal, with an equilibrium concentration of cystine in the solution of 0·54 millimol per liter, to 0·021 millimol per gram of charcoal. In the latter case in the presence of the capillary-active substance there was an equilibrium concentration of 1·1 millimol per liter. The table 2

TABLE 2

Substance.	c (mol. per liter).	$a\left(\frac{\text{millimol}}{\text{g. charcoal}}\right)$.	$\frac{n^2-1}{n^2+2}Mv$.	w.
Amyl alcohol	0·0015	0·87	26·7	7·9
Acetone	0·073	1·33	16·2	8·3
Methyl phenyl-ketone	<0·00035	0·73	36·3	8·0
Acetamide	0·17	1·2	14·9	7·3
Valeramide	0·003	0·62	28·7	6·9
Acetonitrile	0·2	1·5	11·1	7·7
Isovaleronitrile	0·0015	0·83	25·1	7·1
asym. Dimethyl-urea	0·03	1·1	23·3	9·0
sym. Diethylurea	0·002	0·68	32·4	6·9
Phenylurea	0·0002	0·76	37·8	8·6

shows that the equilibrium concentrations of the capillary-active substances in solution are very different, the substances differing markedly in their adsorbability. The adsorbed amounts of a, in millimols per gram of charcoal, are not so very different. The agreement is still better if we compare the surface w calculated as if the molecules were cubes, these cubes

being the volume which is really occupied by the molecules themselves. This true volume, according to the theory of Clausius and Mosotti, is equal to $\frac{n^2 - 1}{n^2 + 2} \mathrm{M}v$. In this expression n is the refractive index of the substance, M its molecular weight and v its specific volume. The base of the cube then becomes

$$\left(\frac{n^2 - 1}{n^2 + 2} \mathrm{M}v\right)^{\frac{2}{3}}$$

and w, the surface really covered by the molecules, is equal to

$$\left(\frac{n^2 - 1}{n^2 + 2} \mathrm{M}v\right)^{\frac{2}{3}} a.$$

There are still other substances which are not capillary-active, but nevertheless retard this reaction still more than the capillary-active ones. One of these substances is hydrocyanic acid. This might seem to be incompatible with the view just given. But Warburg was able to explain this discrepancy and to draw an improved and more subtle picture of the structure on the surface of blood charcoal. He found that the retarding influence of hydrocyanic acid was only shown when the charcoal contained a small amount of iron. His first aim was to prepare a specimen of charcoal that adsorbed amino-acids strongly, without catalyzing their oxidation. An iron-free charcoal made from cane-sugar did not quite fulfil these demands. Contrary to the behaviour of blood charcoal it was quickly oxidized by the air and this reaction induced the oxidation of the amino-acids on the surface. But their

oxidation was not retarded by hydrocyanic acid, and this was already in accord with the view that the presence of iron is necessary to cause this retardation. But an iron-free charcoal, made from cane-sugar, prepared after adding a small amount of a silicate, was found to give the desired results. It adsorbed amino-acids strongly, but did not catalyze their oxidation to

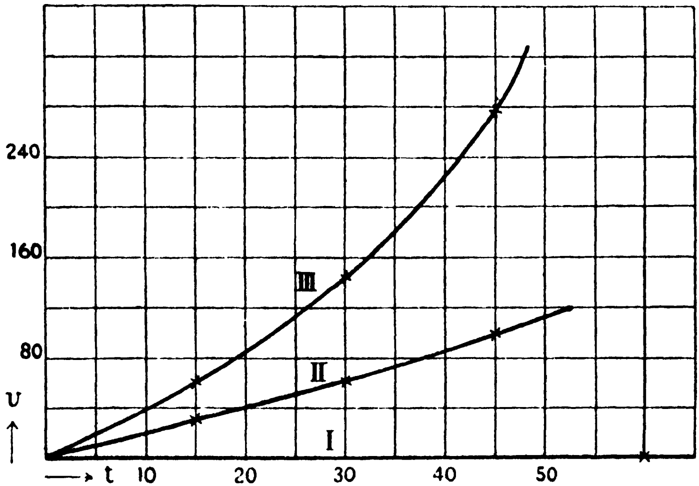

FIG. 3.

any extent. If iron was then added to this charcoal, in a suitable form, the oxidation of the amino-acids was strongly catalyzed, and this effect was completely inhibited by adding hydrocyanic acid. The presence of nitrogen seems to be necessary for the fixation of the iron on the surface, and therefore substances like hæmine or a dyestuff with a small amount of an iron salt act best. Fig. 3 shows the effect of different

additions of hæmine upon the catalytic activity of the charcoal. Curve I refers to an experiment without hæmine, Curve II to one with 0·2 gram of hæmine to 100 grams of sugar, Curve III to one with 2 grams

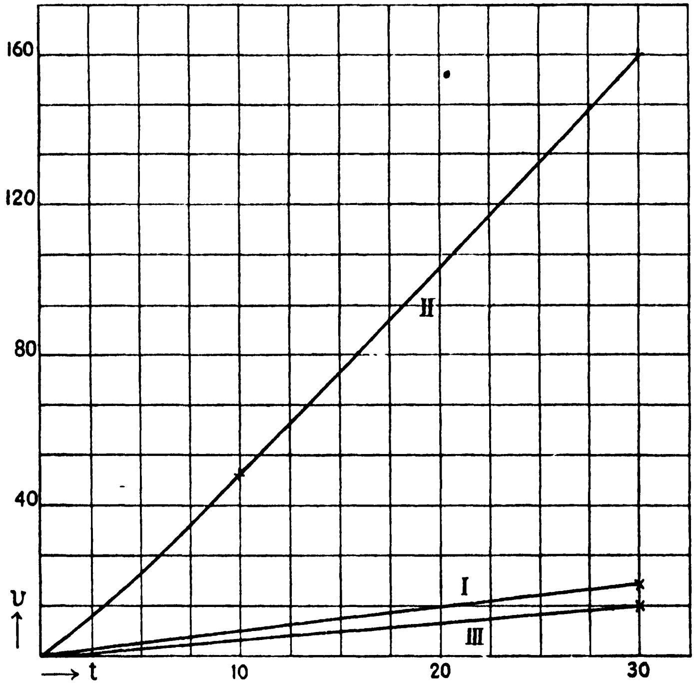

FIG. 4.

of hæmine to 100 grams of sugar. Fig. 4 shows the effect of the addition of hydrocyanic acid which renders the active charcoal totally inactive. Curve I refers to the inactive charcoal, Curve II to the activated charcoal containing 1·25 mg. Fe to the gram of char-

coal, Curve III to the same activated charcoal retarded by HCN. Its concentration was 1 millimol per liter. In both figures the abscissæ are time (in minutes) and the ordinates the amounts of oxygen absorbed (in cubic millimetres). In this way it was possible to synthesize a charcoal with the same qualities as blood charcoal. The iron compound is most likely dispersed on the surface of the charcoal, and therefore the whole surface does not behave as a catalyst. On the contrary, only those spots rich in iron are catalytically active. Hydrocyanic acid retards the catalysis because it has a certain affinity for iron and is probably bound to it in a rather loose reversible union similar to an adsorption. The retarding action of capillary-active substances is not caused by this specific bond. The substances simply cover the whole surface including those portions rich in iron. Warburg was able to prepare charcoals which catalyzed the above reaction even more strongly than blood charcoal, by igniting organic substances containing iron and nitrogen such as hæmine, or a dyestuff like Bismarck brown to which small amounts of an iron salt had been added.

I may add that Warburg [7] used the retarding effect of capillary-active substances, especially the validity of Traube's rule, to decide to what degree biological reactions are surface reactions. He tried to retard them with organic substances belonging to the same homologous series. In many cases he succeeded in doing so, for example in the case of the reactions underlying carbon assimilation, respiration, fermentation and also in the strange reaction, so similar to

fermentation, which goes on, as Warburg has shown, in cancer-cells. In each of these cases he found retarding effects from capillary-active substances. The oxidation of amino-acids for example, cystine, leucine and others by blood charcoal, was a good model of the reaction underlying respiration. The reaction underlying respiration is retarded not only by capillary-active substances but also by hydrocyanic acid, and Warburg therefore considers it to be a reaction proceeding on a surface, but influenced by iron. Fermentation on the other hand is not influenced by hydrocyanic acid but mainly by capillary-active substances.

The examples given thus far show how our conceptions of adsorption must be specialized to explain new results. In other cases well-known features of adsorption compounds lead to consequences which are new and important.

Adsorption causes the molecules of the adsorbent and the adsorbed substance to lie closely packed. This is an important fact in chemical kinetics and one cause of the catalyzing effects of solid surfaces. But it is also of great influence in photochemical phenomena, as was shown recently by Kautsky and Zocher.[8] It especially applies in chemiluminescence. We have good reason to believe, that in most, perhaps in all cases of chemiluminescence, it is not the chemical reaction of the molecules which emits light but rather the transfer of some of the chemical energy from the reacting molecules to neighbouring molecules which are capable of radiation.[9].

Chemiluminescence has therefore a great similarity

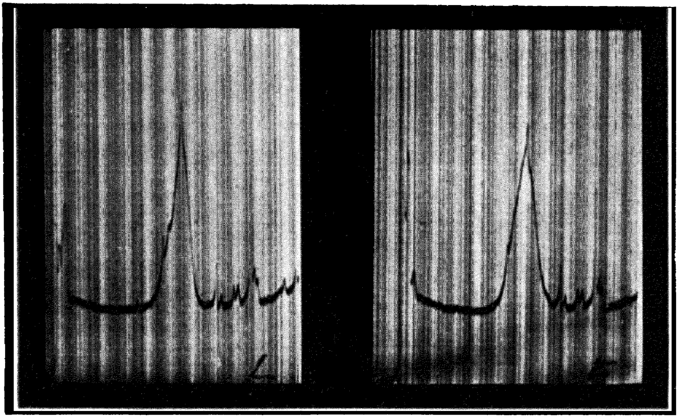

FIG. 5.

to fluorescence. In the case of fluorescence the light entering the system brings the molecules capable of radiation into an active form, richer in energy, and light is emitted when these molecules return to their normal states. In chemiluminescence the energy of the chemical reaction, instead of light energy, causes a similar change in neighbouring molecules and the result is again an emission of light. Kautsky and Neitzke [10] tested this theory in the following manner. It should, they reasoned, be possible to force fluorescent substances to show chemiluminescence by bringing their molecules in close contact with other molecules, which are undergoing chemical reaction. To this end rhodamine dyestuffs which are strongly fluorescent were adsorbed on the surface of solid adsorbents such as silico-oxalic acid $\left(\begin{array}{c}\text{SiOOH}\\ | \\ \text{SiOOH}\end{array}\right)$ or certain silico-oxyhydrides, derivatives of calcium silicide ($CaSi_2$). These compounds are strong reducing agents and their oxidation sets free large amounts of energy. By oxidizing these silicon derivatives, for instance with a permanganate, the dyestuffs adsorbed on their surfaces were made to emit light. This chemiluminescence had exactly the same spectrum as the fluorescent light of the dyestuffs under discussion. As an example, Fig. 5 shows the photometric curves for the chemiluminescence (L) and fluorescence (F) of rhodamine sulphonate.

If this theory has a more general bearing, then the close packing of molecules is an important factor for all cases of chemiluminiscence, and such a close packing

is best obtained in cases of adsorption. It is remarkable indeed that very many chemical reactions, giving chemiluminiscence, proceed in heterogeneous systems, where adsorption is possible, but not in homogeneous ones. In bioluminescence for instance we have, according to the investigations of Dubois and Newton Harvey,[11] many cases where two substances, luciferin and luciferase, are necessary for the emission of light. The latter is colloidal and furnishes the surface necessary for adsorption. It is also the substance capable of radiation. The luciferin on the other hand is the substance which is oxidized and supplies the energy necessary to activate the molecules of the luciferase.

This mechanism of chemiluminescence is the reverse of the mechanism of sensitization, well known in photography. In the latter case light activates molecules of dyestuffs, and they transfer their energy to neighbouring molecules of a different kind and make them reactive. It is evident that here, also, a close packing of the molecules is favourable to this transfer and reactions of this sort are usually found in colloidal systems.[12]

There seems to be one general result which is well established and which may be important when discussing biological questions. It appears that biological processes do not go on as a rule in dilute solutions, but rather they probably proceed in condensed systems, for instance in adsorption-layers. Such reactions in adsorption layers, as those discussed by Warburg, are only one example of reactions in condensed systems. A second type of reaction in a condensed system is the

exchange reaction as shown by the permutites or reactions such as the transformation of cellulose into nitrocellulose. These are chemical reactions of the solid substance which proceed completely and rapidly because of the large interior surface and porous character of the solid. In many cases the solid seems to consist of thin layers or fibres of only one or two molecules thickness. Every molecule of the initial substance is transformed into a molecule of the new substance. Quite a number of such reactions have been found recently by Kohlschütter,[13] Kautsky [14] and others. It therefore is perhaps opportune to give them a name. Such solid substances may be called permutoids, their reactions permutoid reactions.[15] R. O. Herzog [16] has pointed out that they may be of biological importance. Reactions in condensed systems, reactions in adsorption layers and permutoid reactions are, I believe, very frequent in biology. They most likely explain why the organic chemistry of the cells is so very different from the organic chemistry in our test-tubes.

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CHAPTER II

THE ELECTROKINETIC POTENTIAL

THE electrical phenomena with which we have to deal in capillary and colloidal chemistry are very different from those which are well known in electrochemistry. In the latter domain of science we have a large number of experiments on the electromotive force of voltaic cells and electrolysis. Nernst's thermodynamic theory of the electrode potential, and the theory of diffusion and of reaction velocity go a long way in explaining the principal phenomena. In colloidal chemistry we must deal with certain electrical phenomena, which have been neglected in electrochemistry. They are the so-called electrokinetic phenomena, electro-endosmosis, cataphoresis, stream potential and the potential of moving particles. They have of late been studied in so many respects that the chief facts need only be mentioned.

In electro-endosmosis and cataphoresis, an electromotive force acts on an interface, the electric current flowing tangentially to the plane of the interface and causing a movement of one phase with respect to the other. For instance, in electro-endosmosis a fine capillary lies between the electrodes and the electromotive force causes a movement of the fluid through

the capillary; in cataphoresis, on the other hand, the particle of a different phase, either solid, liquid, or gas, is moved through a liquid under the influence of the electric current. In stream potential and the potential of moving particles, the relationship is reversed: the movement of one phase with respect to the other causes an electromotive force. In stream potential a fluid is pressed through a capillary lying between two electrodes and the movement of the fluid causes an electric current to flow from one electrode to the other; in the potential of moving particles, the particles fall, for instance, in a column of liquid and set up an electric current between two electrodes, one at the upper and one at the lower end of the column. That these four phenomena are so closely related, is proved by very trustworthy experiments.

The theory of these electrokinetic phenomena was first given by Helmholtz [1] about fifty years ago. It covered the purely physical facts so well, that until two years ago no correction was found necessary. By applying their theory of strong electrolytes Debye and Hueckel [2] found certain corrections in the theory of Helmholtz. Helmholtz assumed a double layer on the interface between the two phases, and the potential of this double layer—we may call it ζ, in contrast to the ϵ-potential of Nernst—is a characteristic quantity entering into all his formulæ. These are the following: for electro-endomosis we have

$$v = \frac{\zeta r^2 HD}{4\eta}.$$

Here v is the amount of fluid flowing per second through a capillary of radius r under the influence of an external potential gradient H; D is the dielectric constant of the fluid (generally water is used) and η the viscosity of the fluid. I must add here, that Helmholtz did not take account of the dielectric-constant, a point which must be considered more fully later. For cataphoresis Helmholtz wrote $u = \frac{\zeta HD}{4\eta}$ where u is the cataphoretic velocity of the particle, in centimeters per second, which Helmholtz believed to be independent of its shape. Debye and Hueckel showed that this is not the case, but that the numerical quantity in this formula changes with the shape of the particle. For a spherical particle they found

$$u = \frac{\zeta HD}{6\pi\eta}.$$

For the stream potential we have

$$S = \frac{\zeta PD}{4\pi\eta\lambda}.$$

Here S is the potential between the two electrodes caused by the movement of the liquid, P is the pressure with which the liquid is forced through the capillary, and λ is the electrical conductivity of the liquid.

Helmholtz did not discuss the nature of this electrokinetic potential, in so far as it was changed by the addition of electrolytes or non-electrolytes. He believed it to be caused by a double layer, in the true sense of the word, resulting from two electrically

charged layers lying opposite one another at a distance of one molecule. He therefore neglected the influence of the dielectric constant.

The rapid development of electrochemistry since 1887 naturally led to the following question: what relationship exists between the electrokinetic potential, ζ, and the thermodynamic potential of Nernst, ϵ? The first attempt to answer the question came with the reawakening of colloidal chemistry about the year 1900. Billiter [3] tried to explain the electrokinetic phenomena by simply assuming that the electrokinetic potential is identical with the thermodynamic potential. The extraordinary conclusions at which he arrived made this assumption very doubtful. But one idea introduced by Billiter proved to be valuable and has been retained. He did not consider the double layer to be a double layer in the strict sense of the term, but believed it to be "dissociated," a part of the ions of the layer on the liquid side having diffused into the liquid. The charge of the layer therefore does not lie in a plane but in a certain space extending sensibly into the interior of the liquid. It seems to be well established that heat motion must necessarily cause such a dissociation or diffusion of the double layer. As a consequence of the depth of this double layer Pellat [4] introduced the dielectric constant into the Helmholtz formulæ.

To explain the relationship between the electrokinetic potential and the thermodynamic potential, it would be simplest and most direct to measure them both for the same interface. This cannot be done very

easily. The ϵ-potential is best known for metal electrodes; but it is not so simple to determine the ζ-potential for metals. Cataphoretic experiments with metal sols are feasible, but it seems rather doubtful whether the metal surface of colloidal particles may be regarded as identical with the surface of metallic electrodes. Freundlich and Rona [5] preferred to try glass surfaces for comparing the two potentials. Elec-

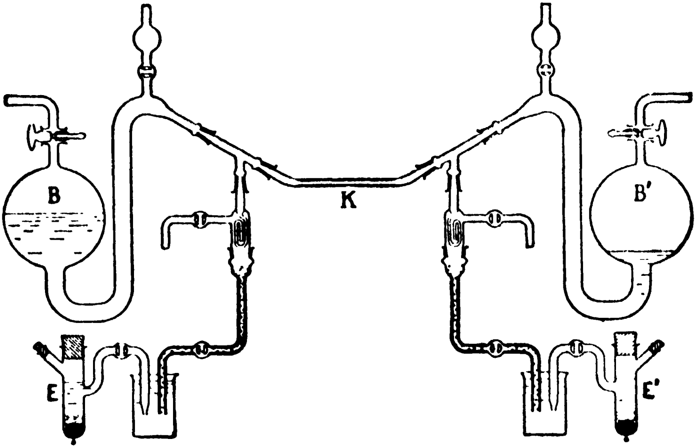


FIG. 6.

tro-endosmosis and especially stream potentials may be measured accurately in glass capillaries and they give the values of ζ, the electrokinetic potential. The above figure (Fig. 6) shows the arrangement as used for these measurements of stream potentials. The fluid was pressed through the capillary K and the potential difference between the two electrodes E and E_1 on either side of the capillary was measured, using

a bridge and a suitable electrometer. The measurement of an ϵ-potential for glass electrodes is not so simple. But this has been accomplished by the experiments of Haber and Klemensiewicz.[6] They dipped a very thin glass bulb, having a wall less than 0·1 mm. thick, into a beaker containing a solution of an electrolyte (Fig. 7). The bulb also contained a platinum electrode immersed in an electrolytic solu-

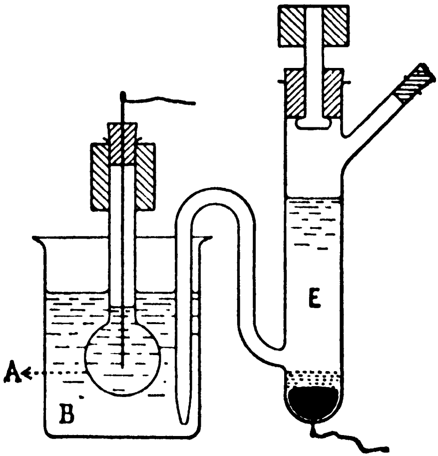
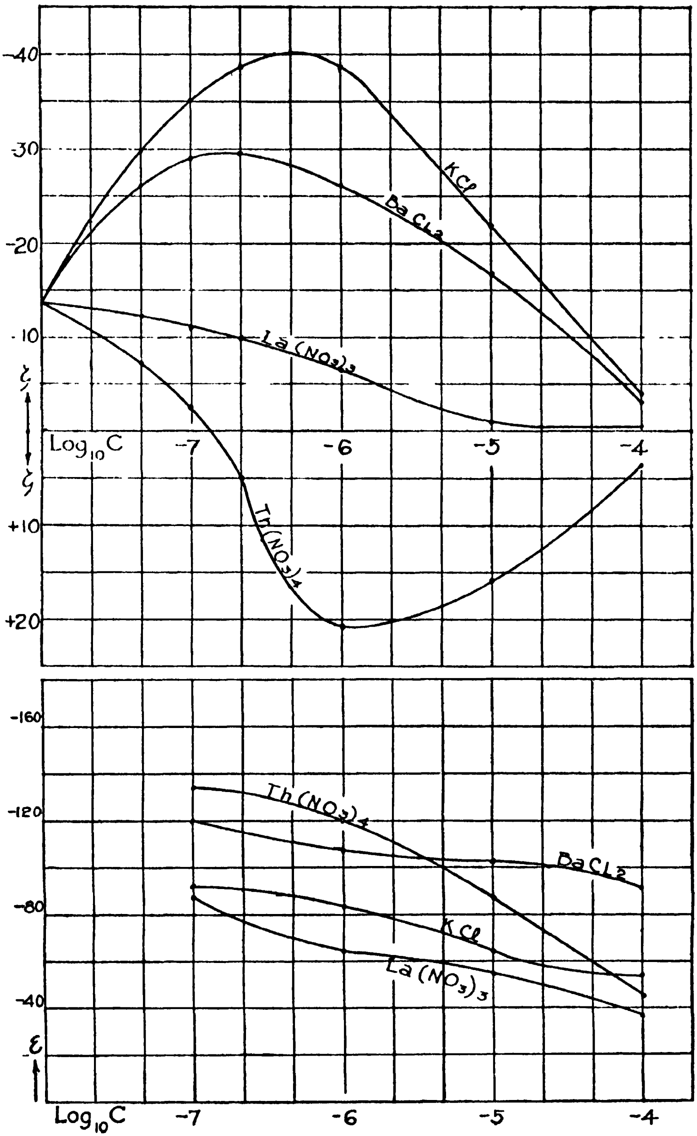


FIG. 7.

tion which remained the same during all the experiments. A normal electrode was immersed in the beaker. The potential difference between the electrodes was measured with an electrometer. If the character and concentration of the electrolytes in the beaker was changed, the potential difference between the glass bulb electrode and the normal electrode changed in a regular way. Haber and Klemensiewicz

found that the glass bulb behaved very much like a hydrogen electrode of constant concentration. In extension of these experiments by Haber and Klemensiewicz new measurements by Horovitz [7] have shown that the glass electrode is not only sensitive to changes of concentration of the hydrogen and hydroxyl ions, but for some kinds of glass also to the change of other ions contained in the glass, especially the cations of the alkalies. In any case, the potential of the glass bulb behaves like a thermodynamic potential and may be compared to the potential of an alloy.

In this way it was possible to compare the ζ-potential of a glass surface with its ϵ-potential. If the potentials are identical or very closely connected, they ought to be influenced by different electrolytes in a similar manner. If this were not the case, they should be considered as being very different and independent of each other. The experiments proved the latter to be true. The outstanding influence of the hydrogen ion, so characteristic of the potential of the glass bulb-electrode, was not specially marked for the ζ-potential. On the other hand, capillary-active substances (dyes, etc.), and ions of high valency changed the ζ-potential greatly, but had no marked effect on the potential difference of the glass electrode. The results of the experiments of Freundlich and Rona were confirmed by the new and more extensive measurements of Ettisch.[8] He compared, for instance, the influence of salts with cations of different valencies. The curves in the following diagrams (Fig. 8) show how very different the ζ- and ϵ-potentials behave. The



-40
-30
-20
-10
ζ
ζ
+10
+20
Log10C
-7
-6
-5
-4
KCl
BaCl2
La(NO3)3
Th(NO3)4
-160
-120
-80
-40
ε
Log10C
-7
-6
-5
-4
Th(NO3)4
BaCl2
KCl
La(NO3)3

FIG. 8.

abscissæ are the logarithms of the concentrations of salt, the ordinates the ζ- and ϵ-potentials. The behaviour of $Th(NO_3)_4$ should be especially noted. It changes the sign of the ζ-potential in very low concentrations (about 10^{-7} mol. per liter), whereas the sign of the ϵ-potential is not changed in a concentration 1000 times as great. A similar series of experiments (Fig. 9) was carried out with salts of certain quinine derivatives, the chlorides of optochine (ethyl-dihydro-cupreine), eucupine (isoamyl-dihydro-cupreine) and vucine (octyldihydro-cupreine), three substances with increasing capillary activity. The difference in the type of the curves, marked respectively *o*, *e*, and *v*, is again very marked. The strongly capillary-active vucine was able to change the sign of the glass in the case of the ζ-potential, whereas nothing similar was observed in that of the ϵ-potential.

These series of experiments were so nearly identical as to surface conditions, that little doubt remains as to the difference in the behaviour of the ζ- and ϵ-potentials; the two potentials are very independent of one another. This may be explained by considering that we are not measuring the same quantity. If we measure the thermodynamic potential ϵ in voltaic cells, we measure the potential in a *vertical* direction between the two phases. The electrokinetic potential ζ, on the other hand, is measured *tangentially* to the interface between the two phases. In the former case, we determine the potential difference between the surface layer of the solid electrode itself and the interior of the liquid, while in the case of the electrokinetic

experiments, we have to assume that a layer of liquid firmly adheres to the solid surface, and on measuring the ζ-potential we determine the potential difference

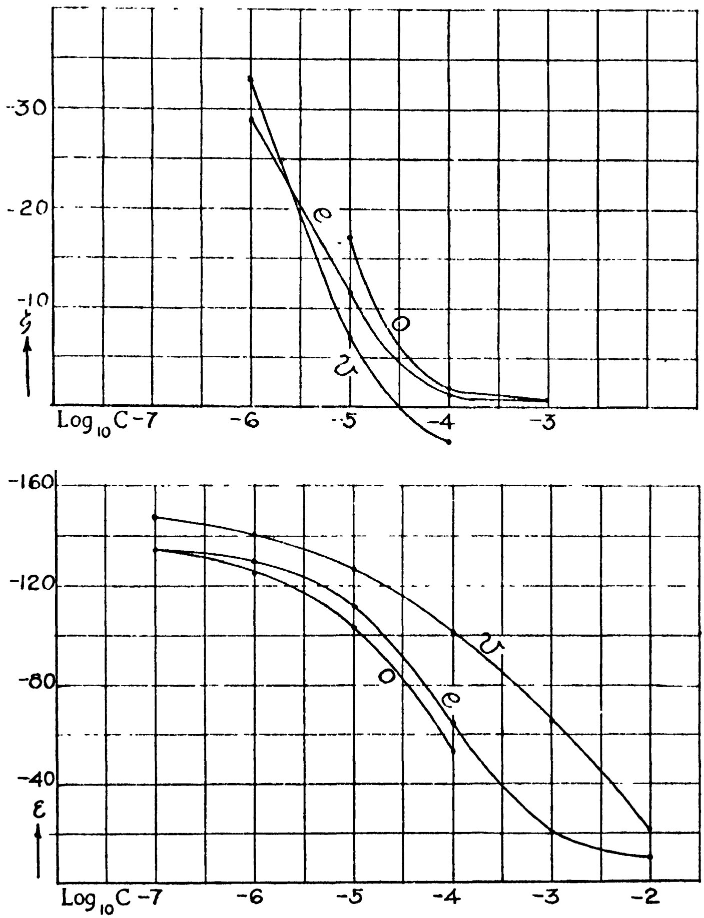


FIG. 9.

between this firmly adhering layer of liquid and the interior of the liquid. There is a movement between two liquid layers, not between the liquid and the solid wall itself. This assumption would be untenable, if we had a double layer in the true sense of the term, as Helmholtz suggested, because there would then be no change of potential between the two layers. But if we assume a dissociated or diffuse double layer, with the electric charge of the one layer not lying in a plane but in a certain space extending sensibly into the interior of the liquid, then there is no difficulty in assuming a potential difference between the adherent layer of liquid and the interior of the liquid itself. The following diagram (Fig. 10) gives a rough picture of this view, the abscissa being the distance from the solid wall, the ordinate the potential ψ. To the left of A, we have the solid wall or the electrode, between A and B the layer of liquid adhering to the wall, and to the right of B, the movable interior of the liquid. The Curves I and II give two possible slopes of the potential curves and show how the ϵ-potential may be the same, whereas the electro-kinetic potential ζ is not only smaller but even different in sign. The ϵ-potential is mainly influenced by those ions which really enter the solid electrode. If we have a metal electrode, the ions of the metal will alone decide its value. In the case of the glass electrode, $H^{\cdot}$-ions and the ions of the alkali metals are specially able to enter the surface of the glass itself. The ζ-potential, on the other hand, is dependent upon all of the ions accumulated in the surface layer, that is to say, all ions (and other substances)

adsorbed at the interface. This explains the fact that capillary-active substances influence the electrokinetic potential so strongly.

O. Stern [9] has discussed this trend of thought more exactly from the standpoint of theory, using the point

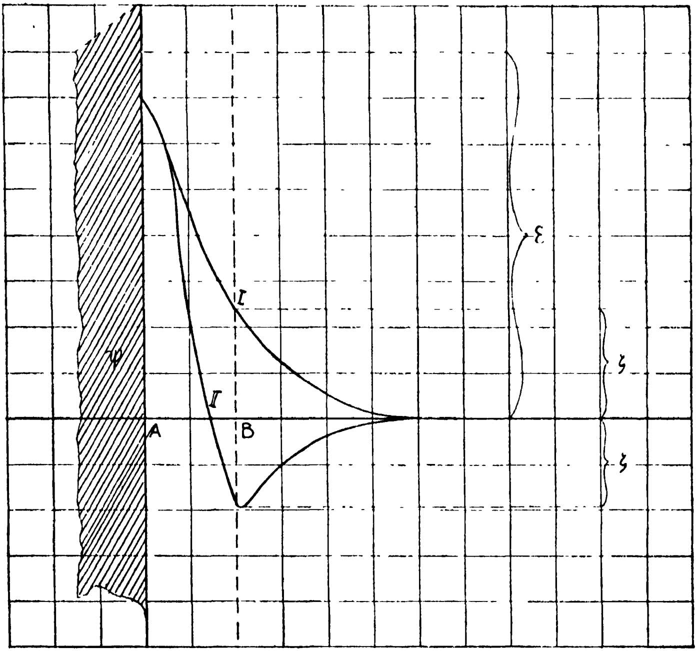


FIG. 10.

of view of Debye and Hueckel. Physicists usually have scruples in assuming an adsorption layer of molecules which is thicker than one molecule. On the other hand, ions may have an adsorption layer of greater thickness Certain facts indicate that the double layer

is not strongly dissociated, the majority of ions being bound to a double layer similar to that assumed by Helmholtz. Only a very small number of ions have diffused into the interior of the liquid. The amount of diffusion and the position of the ions in the neighbourhood of the interface again depends mainly on their

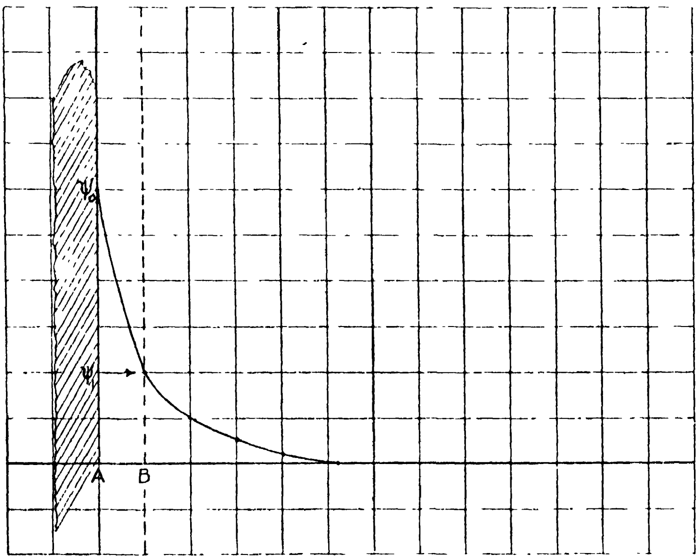


FIG. 11.

adsorption. It is the specific adsorption of each single ion, which has to be introduced. The accompanying figures (11 and 12) give an idea of the views of Stern. The abscissæ are the distances from the solid wall; the ordinates, the potential. In the first figure we have the case in which the adsorbability of the two ions is not very different. ψ_0 is the Nernst potential, ψ_1 the

potential between the layer adhering to the solid and the interior of the liquid. Stern assumes that this layer is only one molecule thick, he therefore identifies ψ_1 with the ζ-potential. The second figure illustrates the case of ions of different adsorbabilities. It is evi-

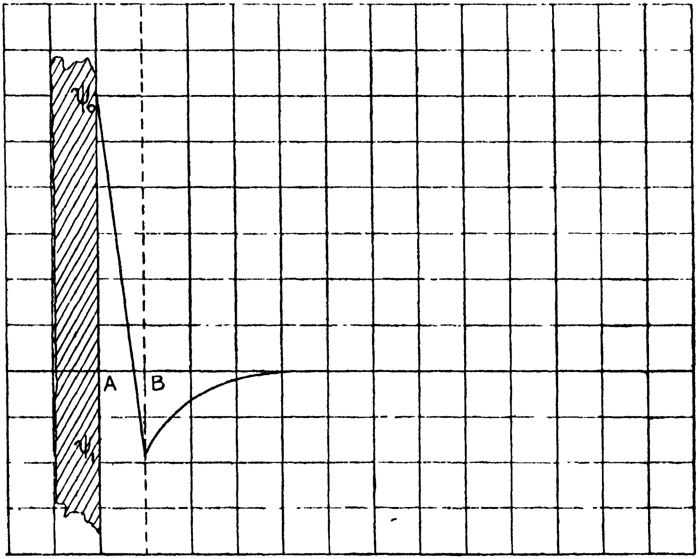


FIG. 12.

dent that ψ_0 is very different from ψ_1, and may even have the opposite sign.

The formula which Stern developed, neglecting many points which are perhaps not negligible, is

$$K_0(\psi_0 - \psi_1) = Fa_s\left[\frac{1}{1+\frac{1}{c}e^{\frac{\Phi^- - F\psi_1}{RT}}} + \frac{1}{1+\frac{1}{c}e^{\frac{\Phi^+ + F\psi_1}{RT}}}\right].$$

Here Φ^+ and Φ^- are the adsorption potentials of the ions, the amount of free energy necessary to transport one molecule of each ion out of the interior of the solution into the interface. Stern regards these quantities as constant. It may be preferable to consider them as a function of the concentration of the ions c and to write in their stead $f^+(c)$ and $f^-(c)$. K_0 is a constant, a_s the maximum amount of ions which may be adsorbed while F, R, and T have their well-known meaning. In any case the formula makes clear that ψ_1 (ψ_1 is identical with ζ) is no simple function of c, and that complicated curves with maxima and minima may result. It is a further consequence of this theory, that the depth to which the double layer extends into the fluid diminishes greatly with growing concentration of the electrolyte. We are not able to calculate the value of ψ_1 as a function of c, because we know nothing about the specific adsorbability of single ions and we do not know the values of $f^+(c)$ and $f^-(c)$. Whoever first finds the way to measure these will also be able to calculate the ζ-c-curves.

So far we have only dealt with the case of an interface between a solid and a liquid. But also in the cases of an interface between two liquids or between a liquid and a gas, the ζ-potential must be distinguished from the ϵ-potential. In the case of the interface between an organic liquid and water the measurements can be made in the following manner. For the ζ-potential, the cataphoresis of small droplets of the organic liquid in the aqueous solution may be used. In order to determine the ϵ-potential, the electromotive force was

determined in cells similar to those used by Beutner[10] and by Baur.[11] The following is a typical arrangement of these cells :—

Normal electrode	Aqueous solution (1) of an electrolyte.	Organic liquid.	Aqueous solution (2) of an electrolyte.	Normal electrode.

The aqueous solution (1) is kept constant, the other is changed and in this way the relative influence of different electrolytes upon the potential of the interface water-organic liquid is measured. Here again the two potentials proved to be independent in certain cases.[12] For instance, with phenol as the organic liquid, $AlCl_3$ reversed the sign of the electrokinetic potential. (These results were compared with the ζ-potential of a KCl solution because a solution of KCl was always used for the aqueous solution (1).) The thermodynamic potential on the other hand was only slightly more negative with $AlCl_3$ than with KCl. The electrode on the $AlCl_3$ side was positive in respect of the electrode on the KCl side.

Frumkin[13] has done some remarkable work on the potential difference between aqueous solutions and the air above them, determining the potential vertically to the plane of the interface. As is shown in Fig. 13, he used a standard solution which he let drop through the interior of the tube A while a second solution was allowed to flow down the inside wall of the same tube. Both liquids are connected to an electrometer by normal electrodes. The dropping solution has the same potential as the surrounding air. The readings on the

electrometer will give a relative value of the potential between the liquid, flowing down the wall of the tube and the air. In order to test this method of measurement Frumkin developed an independent method (Fig. 14). He used a very fine platinum wire C which was held parallel to the surface of the liquid contained in A and heated to incandescence by a small flame. This wire was connected with an electrometer. Under

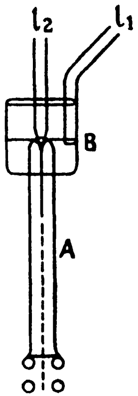


FIG. 13.

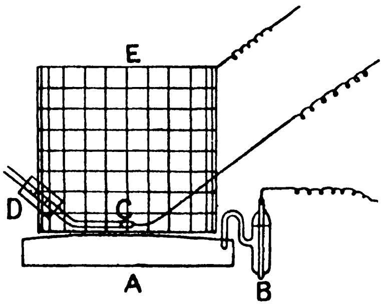


FIG. 14.

these conditions a copious supply of electrons is given off from the wire and it assumes the same potential as the surface of the liquid.[14] If the concentration or nature of the liquid is changed, the reading on the electrometer will change. It may be compensated by an electromotive force introduced between the normal electrode (B) and the earth. The whole is protected by a cage of wire gauze against electrostatic disturbances.

The following table (No. 3) shows the agreement between the two methods:—

TABLE 3

Solution.	Potential in millivolts, measured	
	(a) by using the dropping electrode.	(b) by the flame electrode.
0·0255 mol. $C_6H_5 . COOH$	+ 300	+ 306
8 mol. $CH_3 . COOH$.	+ 284	+ 294
2·8 mol. KCNS . .	− 106	− 98
0·5 mol. $CCl_3 . COOH$.	− 345	− 328

The potentials which Frumkin usually measured by the first method, using the dropping electrode, were found to be absolutely dependent on the composition of the surface layer of molecules limiting the liquid phase. This layer is an adsorption layer, the composition of which may be derived from the changes of surface tension caused by dissolved substances in accordance with Gibbs' adsorption law. Frumkin's experiments agreed excellently with the results which one would expect from adsorption caused by changes in surface tension. The following example illustrates this. Organic substances such as the fatty acids, alcohols, and others caused the outer layer of the surface to become positively charged with respect to the interior of the liquid. As the concentration of the dissolved substance increased, a constant limiting value of the potential was reached. The concentrations of substances, belonging to the homologous series which

produced the same fractional change in potential (one-quarter of the limiting value), were found to follow Traube's rule. This effect is always characteristic of the adsorption of capillary-active substances. The following table (No. 4) gives the values found for a series of fatty acids :--

TABLE 4

Substance.	c (mol. per liter).	$\frac{c_n}{c_{n+1}}$.
Acetic acid . .	0·260	—
Propionic acid . .	0·075	3·47
Butyric acid . .	0·022	3·41
Valeric acid . .	0·0068	3·23
Hexoic acid . .	1·00176	3·87

Since adsorption has such a pronounced influence, it might be felt that the potential between liquid and gas, determined by these methods, might be identical with an electrokinetic potential on the liquid-gas interface. This has been measured by McTaggart.[15] He determined the velocity of cataphoresis for small gas bubbles in aqueous solutions. The ζ-potential obtained in this way was not identical with the potential as measured by Frumkin. In the experiments of McTaggart, the same influence of the ions of high valency was found as in the case of other cataphoretic experiments. The $Th^{\cdot\cdot\cdot\cdot}$-ion, for instance, changed the sign of the charge just as it did in the previously mentioned measurements on stream potential. This influence of high valency was not found by Frumkin.

We therefore may assume in the case of a liquid-gas interface that a part of the electric charge is distributed towards the interior of the liquid, and this causes a ζ-potential in electrokinetic experiments. This does not show up in the experiments of Frumkin, who determined the potential vertically to the interface.

It therefore seems correct to assume a dissociated double layer on every interface, in any case, if a liquid phase is one of the components, and to distinguish systematically between the ζ- and the ϵ-potentials.

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CHAPTER III

ADSORPTION, VALENCY, AND COAGULATION

THE coagulation of hydrophobic sols is a very complicated phenomenon. Although much work has been done during the last twenty years to clarify the subject, we are still rather far trom a thorough understanding of it. Nevertheless the chief paths have been cut through the thicket. We know the main facts and their correlation.

The hydrophobic sols with which we must deal are the colloidal solutions of metals, like gold and silver, of oxides, such as copper oxide, aluminium oxide, iron oxide [1] and of sulphides, such as arsenic trisulphide. These are all very sensitive towards electrolytes, and may therefore be considered as hydrophobic sols, although the sols of aluminium- and iron-oxide have some properties in common with hydrophilic sols. If one investigates the cataphoresis of these sols, their particles show a very distinct charge. The charge is negative for the sols of gold, silver, and arsenic trisulphide, and positive for the oxides of copper, aluminium, and iron.

If an electrolyte be added to a hydrophobic sol and

its behaviour followed under the ultramicroscope, the particles of the sol do not remain a certain distance apart as they do before the addition of the electrolyte. On the contrary as soon as two or more particles come sufficiently close to one another they stick together and form clusters which steadily increase in size and at last settle out of the solution. Two distinct processes operate to bring about this coagulation. First we have the change of the particles caused by the electrolyte which is responsible for the fact that they are able to approach one another more closely and stick together. In the second place the result of this first change is the gathering of the particles into clusters, the pure kinetics of coagulation.

The chief facts concerning the changes in the particles, which cause them to cohere, are the subject of this chapter. However, it will be necessary briefly to discuss the rate of coagulation in order to understand more fully the influence of electrolytes.

If an electrolyte such as sodium chloride be added to a red gold sol the colour of the sol turns violet and then blue in a certain period of time. The reciprocal value of this time is a measure of the rate of coagulation. With increasing concentration c of electrolyte the velocity becomes greater but finally remains constant over the whole range of higher concentrations. This behaviour which was first found by Zsigmondy [2] is shown in Table 5. In this way a range of *slow coagulation* may be distinguished from the range of constant *rapid coagulation.* This rate of rapid coagulation is also independent of the nature of the added electrolyte.

TABLE 5

c (millimoles per litre).	Time of coagulation (in seconds).	
5	150	Range of slow coagulation.
10	12	
20	7·2	Range of rapid coagulation.
50	7	
75	6·5	
100	7	
150	6	
200	6–7	
300	7·5	
500	7	

Smoluchowski [3] developed a theory of the rate of *rapid* coagulation from a kinetic point of view. This theory agrees very well with the facts, as will be shown in the following chapter. He assumes that in this range of rapid coagulation, every collision between two particles, which brings them sufficiently close, is inelastic. The particles attach themselves to one another and do not separate again. In the original sol it is probable that repulsive forces prevent the close approach of the particles (see also p. 46). These forces of repulsion, existing before the addition of electrolytes and acting between the particles of the sol, are most likely caused by the ζ-potential of the electrical double layer. This double layer forms an envelope of ions around each particle and this extends rather deeply into the liquid phase as was discussed in Chapter II. These forces of repulsion are greatly diminished or perhaps totally abolished in the range of rapid coagulation. This explains the fact that every collision is effective and that there are no differences in the nature of the coagulating ions or their concentrations. Smoluchowski, on calculating the rate of *rapid* coagu-

lation from the kinetic view of the Brownian movement, arrived at the following formula :—

$$k_r = 4\pi D l \qquad . \quad . \quad . \quad (1)$$

In this expression k_r is the velocity constant, D the diffusion constant of the particles, and l the distance to which two particles must approach in order that the collision between them becomes effective. There is no factor in this expression which introduces the nature and concentration of the electrolyte.

The rate of *slow* coagulation is much more complicated. Many of these complications may be caused by difficulties of measurement and they will be discussed in detail later. If these difficulties are eliminated the following expression, developed by Smoluchowski, seems to hold for the rate of slow coagulation :—

$$k_s = 4\pi D l \xi \qquad . \quad . \quad . \quad (2)$$

This equation is only distinguished from equation (1) by the factor ξ, which means that a certain fraction ξ of all collisions are effective in coagulation. This fraction ξ depends very markedly upon the nature and concentration of the electrolyte. The influence of the concentration will be discussed in the following chapter. At this point we are only interested in the influence which the nature of the electrolyte shows.

In order to study this influence it would be most rational to compare the concentrations of electrolyte which produce the same value of ξ and therefore the same value of k_s. In very few cases has this been done.[4] Generally investigators were obliged to compare similar points on the coagulation curves. They

measured for instance those concentrations of electrolytes which produced the same amount of coagulation in a definite period of time. These concentrations will be referred to as *coagulation values* and designated by the symbol γ.

The influence of the nature of the electrolytes, as shown by these coagulation values, proves that we are dealing with an electrical phenomenon. The ions which are the most effective are those having a charge opposite to that of the colloidal particles and the adsorbability and valency of these ions is of great importance. The following tables (next page) give evidence which supports this view. They contain a number of coagulation values γ for the negative arsenic trisulphide sol, and the positive iron oxide sol. The remarkable influence of the cations on the coagulation values of arsenic trisulphide and of the anions in the case of the iron oxide sol, is fully apparent.

The experimental evidence given in these tables points to a direct relationship between coagulation and the electrokinetic properties of the colloids as determined in cataphoretic experiments. This relation will become clearer when we compare the coagulation values with the concentrations of electrolytes which cause the same lowering of the ζ-potential (measured by cataphoretic velocity). Fig. 15 gives the results obtained by Zeh [5] and shows the change in ζ-potential of an arsenic trisulphide sol, upon the addition of a number of complex cobalt salts which give cations of different valencies. The abscissæ are the concentration c in micromoles ($= 1/1000000$ mol.) per liter, the

TABLE 6

γ-VALUES OF AN ARSENIC TRISULPHIDE SOL (NEGATIVE)

Electrolyte.	γ (millimoles per liter).
NaCl	51
KCl	49·5
KNO_3	50
$\frac{K_2SO_4}{2}$	65·5
NH_4Cl	42
HCl	31
Aniline hydrochloride	2·5
Morphine hydrochloride	0·42
New fuchsine	0·11
$MgCl_2$	0·72
$CaCl_2$	0·65
$SrCl_2$	0·635
$BaCl_2$	0·69
$UO_2(NO_3)_2$	0·64
$AlCl_3$	0·093
$\frac{Al_2(SO_4)_3}{2}$	0·096
$Ce(NO_3)_3$	0·080

TABLE 7

γ-VALUES OF AN IRON OXIDE SOL (POSITIVE)

Electrolyte.	γ (millimoles per liter).
NaCl	9·25
KCl	9·0
$\frac{BaCl_2}{2}$	9·65
KBr	12·5
KI	16
KNO_3	12
HCl	$>$400
$\frac{Ba(OH)_2}{2}$	0·42
K_2SO_4	0·205
$MgSO_4$	0·22
$K_2Cr_2O_7$	0·195

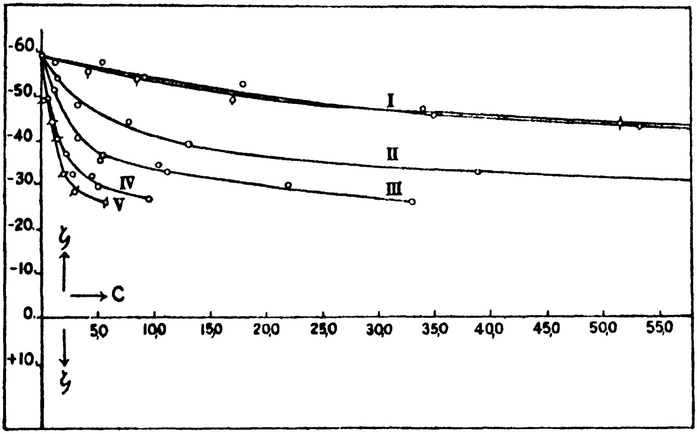


FIG. 15.

ordinates the ζ-potential. The curves marked I refer to the two univalent cations, II to the bivalent, III to the trivalent, IV to the quadrivalent, and V to the sexvalent cation, all mentioned in Table 8. In this table the concentrations c_e, derived for a potential of 64 millivolts, are compared with the coagulation values γ for the same salts. The parallelism is complete. The same holds true for a comparison of the c_e- and γ-values of an iron oxide sol. The c_e-values refer to a ζ-potential of 40 millivolts. Here a series of complex cyanide anions were used and the results are given in Table 9.

It is evident from these tables that the first change in the particles which results in their sticking to one another after collision is caused chiefly by changes in their electrical properties. The potential of the par-

ticles must be lowered to a certain critical value in order that slow coagulation may proceed. It must be practically zero to have rapid coagulation. Coagula-

TABLE 8

Electrolyte.	c_e (micromoles per liter).	γ (micromoles per liter).
$\left[Co(NH_3)_4(NO_2)_2 \begin{smallmatrix}(1)\\(6)\end{smallmatrix}\right]Cl$ . .	59	1290
$[Co(NH_3)_4CO_3]NO_3$	58	1185
$[Co(NH_3)_5Cl]Cl_2$	9	118
$[Co(NH_3)_6]Cl_3$	2·1	25·6
$\left[(NH_3)_4Co\begin{smallmatrix}NH_2\\OH\end{smallmatrix}Co(NH_3)_4\right]Cl_4 . 4H_2O$	1·2	11·4
$\left[Co\left\{\begin{smallmatrix}OH\\OH\end{smallmatrix}Co(NH_3)_4\right\}_3\right]Cl_6$ . .	1·0	8·0

TABLE 9

Electrolyte.	c_e (micromoles per liter).	γ (micromoles per liter).
$Au(CN)_2K$ . . .	320	13200
$Au(CN_4)K$ . . .	25·5	1170
$Pt(CN)_4K_2$ . . .	17	390
$Cu(CN)_4K_3$ . . .	9	61
$Fe(CN)_6K_3$ . . .	3·9	31·5
$Fe(CN)_6K_4$ . . .	3·1	15

tion values are therefore an indirect measurement of concentrations which cause the same changes in the ζ-potential.

In order to explain the influence of ions upon the ζ-potential we must refer to Chapter II as mentioned before. Here it was shown that the ζ-potential was caused by the extension of the double layer at the surface of particles into the medium itself. It was shown further that the extension of this double layer is diminished markedly, if the concentration of electrolytes in the medium rises. Haber [6] has explained how the stability of a hydrophobic sol depends on the behaviour of this double layer. When the double layer or ionic envelope extends for some distance into the medium, the particles are unable to approach each other closely. If two particles do approach each other, the ionic envelopes are distorted and this sets up forces of repulsion. They are caused chiefly by osmotic influence because the ions have a tendency to regain their symmetric positions around the particle. These forces of repulsion prevent any close approach. Such are the conditions existing in the sol before the addition of an electrolyte. If now an electrolyte be added, the ζ-potential is lowered so that the depth of the double layer is reduced. The particles may therefore approach much more closely to one another. The distortion of the envelope of ions then causes an asymmetry in the electrical charges, and attractive forces are therefore set up which hold the particles together.

According to the theory of the ζ-potential as developed in the last chapter, the adsorption of any ions at the interface causes a change in this potential. As yet it has not been found possible to calculate the ζ- c-curves, because the adsorption of single ions has

not been satisfactorily measured. Furthermore, we do not know the mutual effects of ions upon each other. However, there is no doubt that, in coagulation, adsorption of ions most certainly occurs. The ion with a charge opposite to that of the colloidal particles before coagulation, is practically always found in the coagulum.

Since the exact relations between adsorption of ions and their effect upon the ζ-potential are not known, it becomes necessary to make certain assumptions with regard to them. It is assumed first that the ions of opposite charge are adsorbed so strongly that the influence of the other ion may be neglected. It is further assumed that *equivalent* amounts of adsorbed ions of opposite charge cause the same lowering of the ζ-potential. Equivalent amounts ought, therefore, to be adsorbed at the coagulation values.[7] This may be true as long as the amounts adsorbed are very small, and as long as we are dealing with ions which do not show specific orientation upon the surface. These assumptions will be found sufficient to explain the fact that ions of the *same* valency but of different adsorbability have such different coagulation values. A comparison of the γ-values in Table 6 with the adsorption curves in Fig. 16 illustrates this fact very well when univalent inorganic cations like the NH_4-ion and organic cations like those of morphine and new fuchsine are compared. Fig. 16 shows the adsorption curves of these cations using As_2S_3, prepared from an arsenious sulphide sol, as adsorbing substance.[8] The abscissæ are the concentrations c in the solution, the ordinates the amounts adsorbed a. Curve I refers to NH_4-ion,

Curve II to the cation of morphine, Curve III to that of new fuchsine. It is evident that the values of c belonging to equivalent amounts adsorbed, show among themselves differences of the same degree as the γ-values in Table 6. Table 10 shows further that in reality the amounts adsorbed by the particles of an As_2S_3-sol for

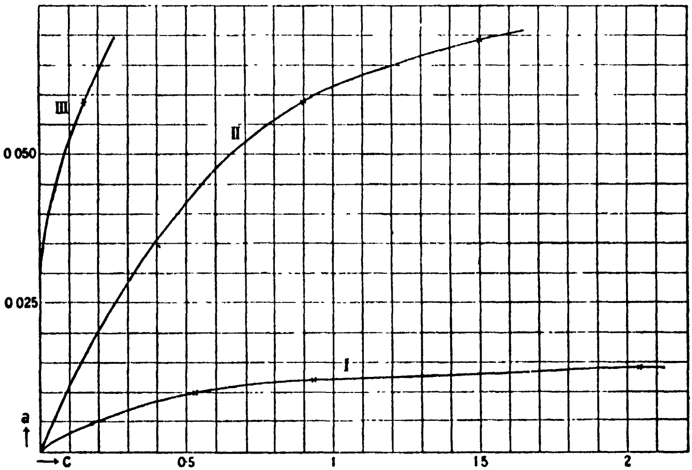


FIG. 16.

different cations at the point of rapid coagulation are practically equivalent. They are calculated in milli-equivalents, per gram of As_2S_3.

TABLE 10 [9]

Cation.	a.
$C_6H_5NH_3^{\bullet}$	0·074
Cation of new fuchsine . . .	0·076
$UO_2^{\bullet\bullet}$	0·088
$Ce^{\bullet\bullet\bullet}$	0·069

The most striking effect, which shows that we are really dealing with adsorption, is the validity of Traube's rule. It only holds exactly in the case of non-electrolytes and weak electrolytes. Frumkin,[10] however, found that a series of strong electrolytes, such as monoethylammonium chloride, diethyl ammonium chloride and so on, exhibit distinctly regular sequences in the change of the potential for the solution-air interface. The similarity to Traube's rule is marked but the ratios are smaller. Table 11 shows

TABLE 11

Substance.	c.	$\frac{c_n}{c_{n+1}}$.
Amines.		
NH_3	2·66	—
$C_2H_5NH_2$ . . .	0·23	11·6
$(C_2H_5)_2NH$ . . .	0·0206	11·2
$(C_2H_5)_3N$	0·00223	9·2
Amine Salts.		
$C_2H_5NH_3Cl$ . . .	2·2	—
$(C_2H_5)_2NH_2 . \frac{SO_4}{2}$ . .	0·57	3·9
$(C_2H_5)_3NHCl$ . . .	0·275	2·1
$(C_2H_5)_4NCl$ . . .	0·34	—

the concentrations of the salts as compared to the concentration of their amines necessary to cause the same change in potential,[11] i.e. 150 millivolts for the amines, 120 for the amine salts.

Very similar results were found for the coagulation

of arsenic trisulphide sols by the same salts. This is shown in Table 12.

TABLE 12

Electrolyte.	γ (millimoles per liter).	$\frac{\gamma n}{\gamma n+1}$.
NH_4Cl	35	—
$C_2H_5NH_3Cl$	18·2	1·9
$(C_2H_5)_2NH_2Cl$	10	1·8
$(C_2H_5)_3NHCl$	2·8	3·5
$(C_2H_5)_4NCl$	0·89	3·1

In order to explain the great differences in coagulation by ions of *different* valency it is not necessary to assume that the ions of higher valency are more strongly adsorbed than those of lower valency. If they were adsorbed equally in equimolar solutions there would still be found this marked difference in the coagulation values. In Fig. 17 the adsorption isothermal refers to *equimolar* solutions having univalent, bivalent, and trivalent ions respectively. It is evident from this curve that adsorption of *equivalent* amounts of the three ions requires a very much lower concentration of the bivalent and trivalent ion than of the univalent one. The order of these concentration values is the same as noted in the coagulation values.

If the relation given in Fig. 17 holds, then an adsorption isothermal should be found when the abscissæ are the coagulation values for uni-, bi-, and tri-valent ions and the ordinates are the relative amounts adsorbed in the ratios one to one-half to one-third.

Since the adsorption isothermal is usually expressed by the formula

$$a = \alpha c^{\frac{1}{n}} \quad \text{or} \quad \log a = \log \alpha + \frac{1}{n} \log c$$

where α and $\frac{1}{n}$ are constants, a straight line should result, if the logarithms of the relative amounts ad-

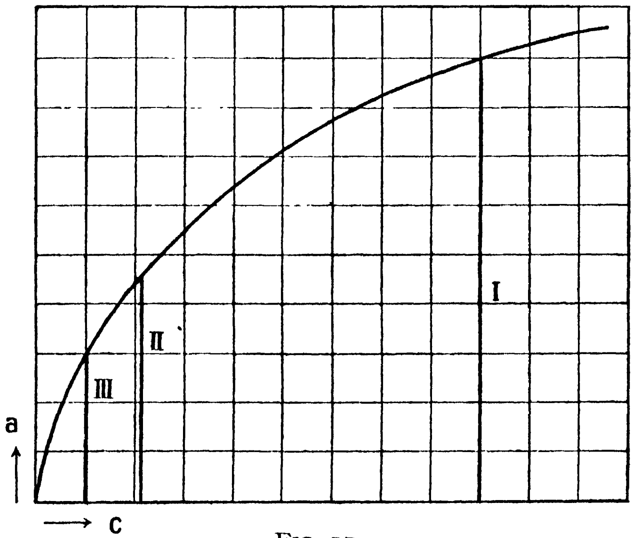


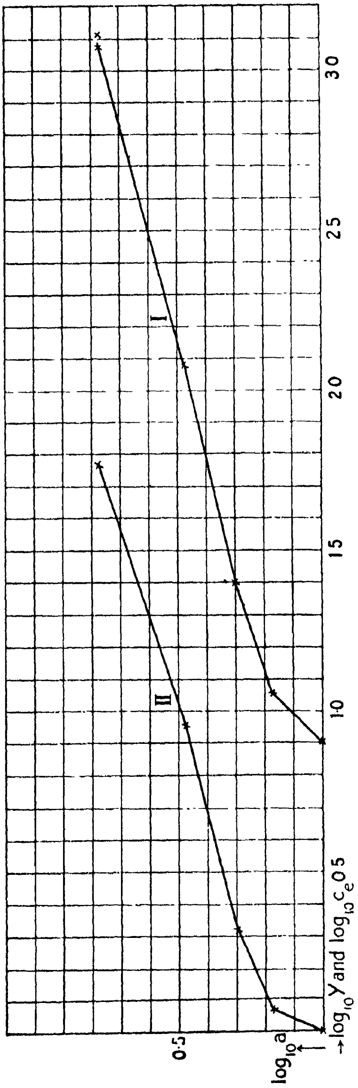
FIG. 17.

sorbed are plotted against the logarithms of the coagulation values γ.[13]

Equal adsorption of ions in equimolar concentrations seems to exist in the case of the complex cobalt ions which were mentioned above (p. 45). Matsuno[14] was the first to show that a great number of these cations, having valencies from one up to six, agree

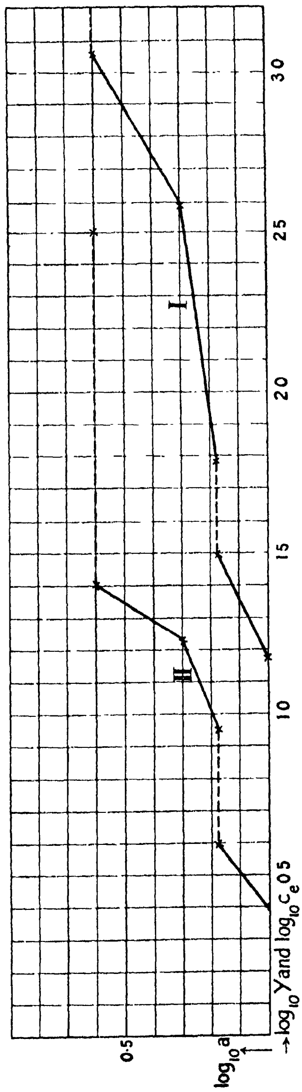
excellently with this hypothesis. His results were closely confirmed by the above-mentioned experiments of Zeh. Zeh, as mentioned, measured not only the coagulation values of these ions for arsenic trisulphide sol but also their influence on the cataphoresis of this sol. Because the concentrations of electrolytes, which cause the same lowering of the ζ-potential, behave exactly as the coagulation values, the results ought to fit the above hypothesis. Fig. 18 shows that this is indeed the case for uni- to quadrivalent ions. In the logarithmic diagram Curve I shows the results for the coagulation values γ and Curve II the results for the concentrations c_e, causing the same lowering of the ζ-potential in cataphoresis. They are straight lines for the uni-, bi-, tri-, and quadrivalent ions.[15]

If the complex cyanides, mentioned above, be used for the coagulation of an iron oxide sol and the influencing of its cataphoretic velocity, it will be noted that they do not fit in equally well with the above hypothesis. In Fig. 19 the results for the iron oxide sols are treated in the same manner as were those for the arsenic trisulphide. The values for the three ions $Au(CN)_4$, $Pt(CN)_4$, and $Cu(CN)_4$ are perhaps in agreement with the adsorption isothermal. But there is a great difference between the two univalent ions $Au(CN)_2$ and $Au(CN)_4$ and also between the two trivalent ions $Cu(CN)_4$ and $Fe(CN)_6$. An explanation of this discrepancy might be found if there was a difference in the adsorbability of the two pairs of ions respectively. $Cu(CN)'''_4$-ion is indeed adsorbed less than $Fe(CN)_6'''$-ion [16] by the particles of an iron oxide sol, prepared



I
II
0·5
1·0
1·5
2·0
2·5
3·0
$\log_{10} a$
$\log_{10} Y$ and $\log_{10} c_e$ 0·5

FIG. 18.



I
II
0·5
1·0
1·5
2·0
2·5
3·0
$\log_{10} a$
$\log_{10} Y$ and $\log_{10} c_e$ 0·5

FIG. 19.

by hydrolyzing $FeCl_3$. But the particles of this sol are not identical with those of the sol used for the experiments in Fig. 19 ; this was prepared by oxidizing $Fe(CO)_5$ with hydrogen peroxide (see reference [1]).

The results given so far in this chapter seem to be true only for very dilute solutions of the electrolytes. It may be remarked that the concentrations were mostly below one millimole per liter. For electrolytes having much higher coagulation values for instance, it should be noted that the parallelism between coagulation values and the influence upon cataphoresis does not seem to hold exactly. Powis [17] pointed out that KCl coagulated As_2S_3-sol in a concentration where the critical value of the ζ-potential had not been reached. We are dealing most likely with a dehydrating effect of the electrolytes as will be discussed in Chapter V. It should also be noted that cases are known in which the structure of the adsorbed ion makes itself felt. The picrate ion is remarkable because it usually requires a smaller amount of adsorbed substance to produce the same coagulation value.[18] It behaves as if it were a bivalent ion instead of univalent. Exactly the same anomaly is found for the activity coefficient of the picrate ion. It was found to be very large in order to account for the dissociation of picric acid.[19] Bjerrum [20] has explained such high activity values as being due to a very asymmetrical structure of the ion, in which the electrical charge is located at some distance from the centre of the ion. Such an asymmetrical univalent ion will behave somewhat like a bivalent one because of its stronger external field.

CHAPTER III. REFERENCES

1. It is not correct to name the well-known sol prepared by hydrolyzing $FeCl_3$ an iron oxide sol. According to the investigations of PAULI (PAULI and MATULA, Kolloidzeitschr. **21**, 49 (1917); PAULI, *ibid* **26**, 20 (1920)), and especially new experiments by BÖHM (Zeitschr. f. anorg. u. allg. Chem. **149**, 203 (1925)), the particles in the sol are mostly a basic iron chloride. In old sols also particles of the hydroxide FeOOH are found crystallizing in the form of goethite. BÖHM used the X-ray method for identifying the particles contained in the sol. Only for the sake of brevity the sols are called sols of iron oxide. The iron oxide sols mentioned in Table 7 and on p. 38 were prepared by hydrolyzing $FeCl_3$. The sol mentioned in Table 9 and in all experiments made by ZEH, was prepared by oxidizing iron carbonyl $Fe(CO)_5$ with hydrogen peroxide (FREUNDLICH and WOSNESSENSKY, Kolloidzeitschr. **33**, 222 (1923)). According to BÖHM this sol contains mainly particles of goethite.
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3. v. SMOLUCHOWSKI, Physik. Zeitschr. **17**, 557; 583 (1916); Zeitschr. f. phys. Chem. **92**, 129 (1917).
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5. FREUNDLICH and ZEH, Zeitschr. f. phys. Chem. **114**, 65 (1924).
6. HABER, Journ. of the Franklin Institute, 1925, S. 450 *et seq*.
7. The view, here preferred, according to which the ζ-potential changes chiefly with the amount of adsorbed ions, is not the only possible one, perhaps not even the correct one. In the end it is probable that the changes in the ζ-potential depend more on the attenuation of the ionic envelope at higher electrolyte concentrations. The ζ-values, which are compared at a given coagulation

value, would then not be such as correspond to equivalent quantities of adsorbed ions, but such as belong to a certain equal thickness of the ionic envelope. To decide whether either view alone is valid, or whether the two can be brought into connexion, will require further experiments.

8. FREUNDLICH, Zeitschr. f. phys. Chem. **73**, 385 (1910).
9. Measurements by FREUNDLICH, Kolloidzeitschr. **1**, 321 (1907), and Zeitschr. f. phys. Chem. **73**, 385 (1910). Strictly comparable are only the two first and the two last numbers which were determined with the same sol.
10. FRUMKIN, Zeitschr. f. phys. Chem. **111**, 190 (1924).
11. The ratio for the amines has a value of about 10 and not of about 3 as in Table 1, because each amine is distinguished from the following one by a C_2H_5-group, i.e. by two CH_2-groups.
12. Unpublished results by Miss V. BIRSTEIN. The difference in the behaviour of the tetra-ethyl salt in Tables 11 and 12 is remarkable, and deserves further investigation.
13. It would be more exact to subtract from these γ-values the amounts adsorbed. For the γ-values are total concentrations and the adsorption isotherm refers to equilibrium concentrations, not to total concentrations.
14. MATSUNO, Journ. Coll. Science, Tokyo, **41**, Nr. 11 (1921).
15. The sexvalent cation shows for the γ and the c_t-values a distinct deviation from the straight line. This was not the case in the experiments of Matsuno. The cause for this discrepancy could not be found as yet.
16. HERMANN HABER, Beitrag z. Kenntnis d. Flockung u. Adsorption hydrophober Sole. Dissertation. Berlin 1925.
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19. v. HALBAN und EBERT, Zeitschr. f. phys. Chem. **112**, 359 (1924).
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CHAPTER IV

THE RATE OF COAGULATION

IN Chapter III it was shown that the change in the colloidal particles, which causes them to adhere to one another, is an electrokinetic phenomenon. The velocity with which the changed particles unite was only discussed in so far as it became necessary for a clear understanding of the electrical changes. In the present chapter this rate of coagulation will be the principal subject of discussion.

It is no easy task to measure the rate of coagulation. The most direct method is to count the particles of a sol in the ultramicroscope and follow the change in their number after the addition of an electrolyte. This has been done for instance by Zsigmondy [1] for gold sols and by Kruyt and A. E. van Arkel [2] for selenium sols. The difficulties of this method arise from the fact that no amicrons should be present.[3] Furthermore, it is not easy to follow the change over a large range of numbers. A rather less direct method may be used for the sol of copper oxide. This colloidal solution is easily prepared by Bredig's method of electrical disintegration.[4] The amount of copper in colloidal solution may be analysed by dissolving the sol in acetic

acid, adding potassium iodide and titrating the amount of iodine set free. In order to separate the coagulated particles from those which are not coagulated a portion of the sol is centrifuged from time to time. The larger coagulated particles are thus removed, and the amount of copper remaining in solution corresponds to the amount of primary, or uncoagulated particles. In many other cases even more indirect methods were used, for instance, the changes of colour. In gold sols this is easy because they change from red to blue.[5] In colloidal solutions of sulphur, or of As_2S_3, where this change is not so marked, a photo-electric cell is suitable for measuring the change of light-absorption.[6] Other sols more related to the hydrophilic sols, such as the colloidal solutions of iron oxide or aluminium oxide, change their viscosity markedly during coagulation. Therefore the rate of coagulation may be measured by determining the rate at which the viscosity changes.[7] It should be noted at this point that the methods which follow the change of primary particles are much more exact than those which depend upon a change in the coagulated particles. The nature of the coagulated particles may depend upon the character and concentration of the coagulating electrolyte.

It has been shown in the last chapter that we must distinguish between a range of constant rapid coagulation, which is reached by higher concentrations of electrolytes, and a range of slow coagulation in which low concentrations of electrolytes are used. It was also mentioned that Smoluchowski had developed a theory of **rapid** coagulation, from a kinetic point of

view, assuming that every collision resulted in coagulation. From this assumption the total number of particles $\Sigma\nu$ diminishes according to a reaction of the second order.

$$-\frac{d\Sigma\nu}{dt} = k_r(\Sigma\nu)^2 \quad . \quad . \quad . \quad (1)$$

Integration gives

$$k_r = \frac{1}{t}\left(\frac{1}{\Sigma\nu} - \frac{1}{\nu_0}\right) \text{ or } \Sigma\nu = \frac{\nu_0}{1+k_r\nu_0 t} \quad . \quad (2)$$

In this expression ν_0 is the number of particles present at the beginning of coagulation, k_r is a constant, and t the time elapsed. As mentioned above we also have

$$k_r = 4\pi Dl \quad . \quad . \quad . \quad (3)$$

For the change in the number of primary particles ν_1 the following expression may be deduced :—

$$\nu_1 = \frac{\nu_0}{(1+k_r\nu_0 t)^2} \quad . \quad . \quad . \quad (4)$$

The changes in the total number of particles $\Sigma\nu$, the primary particles ν_1, and the double particles ν_2, are given by the following curves (Fig. 20). Here the abscissæ are relative values of time, the time t being divided by the so-called period of coagulation $\theta = \frac{1}{k_r\nu_0}$. The ordinates are relative values of the numbers of particles, these numbers being divided by the number ν_0. The extent to which the theory agrees with the facts is shown by the following table. The measurements were made with a gold sol, counting the particles in the ultramicroscope.

TABLE 13

$\nu_0 = 0{\cdot}552 \times 10^{10}$; $r = 24{\cdot}2\mu\mu$; $\frac{l}{r} = 3{\cdot}12$; $k_r = 0{\cdot}02315$

t.	ν_1 (obs.).	ν_1 (calc.).
0	1·97	1·97
2	1·35	1·65
5	1·19	1·31
10	0·89	0·93
20	0·52	0·54
40	0·29	0·25

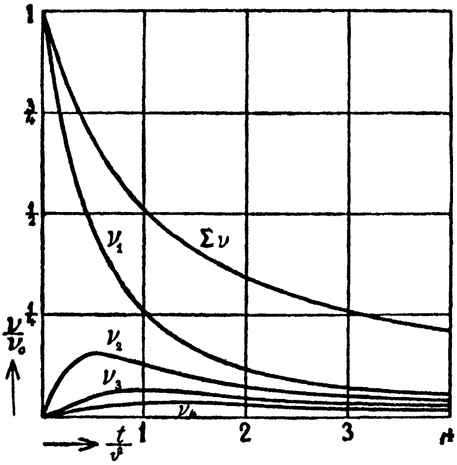

FIG. 20.

The influence of temperature is also in good agreement with the theory. According to the theory of the Brownian movement

$$D = \frac{RT}{6\pi N\eta r} \quad . \quad . \quad . \quad (5)$$

Here N is Avogadro's number, η is the constant of viscosity, r the radius of the particles which are considered to be spherical. If this value of D is introduced into formula (3) one obtains

$$k_r = \frac{2}{3}\frac{RTl}{N\eta r} \quad . \quad . \quad . \quad (6)$$

It may be easily shown that $\frac{T}{\eta}$ is the only term strongly influenced by the temperature, and k_r ought therefore to be proportional to $\frac{T}{\eta}$:

$$k_r = A_r \frac{T}{\eta} \quad . \quad . \quad . \quad . \quad (7)$$

Here A_r is a constant. Experiments by Lachs and Miss Goldberg [8] with gold sols show that this formula indeed holds good.

The rate of **slow** coagulation, on the other hand, is not so easy to explain as the case of rapid coagulation. It is perhaps just as important as the former because, in biological and technical reactions, we have to deal with slow coagulation and not with rapid coagulation.

Two points in the behaviour of slow coagulation are rather striking. In the first place the velocity-curves are often of an autocatalytic type since the coagulation proceeds at first very slowly, then rises quickly and falls off again. In the second place the influence of the concentration of the electrolyte is remarkable because the constant of velocity is proportional to a high power of this concentration.

The first point is more or less accidental and is caused

by the methods used for measuring it. Slow coagulation has hardly ever been measured directly under the ultramicroscope, but nearly always by one of the indirect methods previously mentioned. These methods generally do not permit of the observation of the first small change which is the combination of primary particles to form double particles. This leads to the impression that there is practically no change at the beginning. It would be too wide a digression to consider the details of this question, but it should be pointed out that in many cases this error could be avoided. By stirring vigorously, for instance, the double particles form larger particles more rapidly than do the primary particles,[9] and as a result a sharper separation is obtained by the centrifuge. The autocatalytic character of the coagulation-velocity curve is thus made to disappear and a normal slope such as is found in the case of rapid coagulation results. In Fig. 21 Curve I shows the coagulation velocity of a copper oxide sol without stirring and Curve II shows the effect of stirring. The abscissæ are the time t in minutes, the ordinates the concentration n_1 of the copper oxide sol. The rate of coagulation in Curve II can be calculated according to equation (4). This shows that we are dealing with the rate of the change of the number n_1 of primary particles.[10] Smoluchowski emphasized this fact and characterized the rate of slow coagulation by the formula mentioned in Chapter III :—

$$k_s = 4\pi Dl\xi \quad . \quad . \quad . \quad (8)$$

It is distinguished from the formula (3) for rapid co-

agulation only by a factor ξ which means that every collision between the particles is not effective. ξ gives the fraction of collisions that are effective.

It has been shown in Chapter III that ξ depends absolutely upon the nature of the electrolyte. This influence was further shown to be correlated with the changes in the ζ-potential occurring upon the

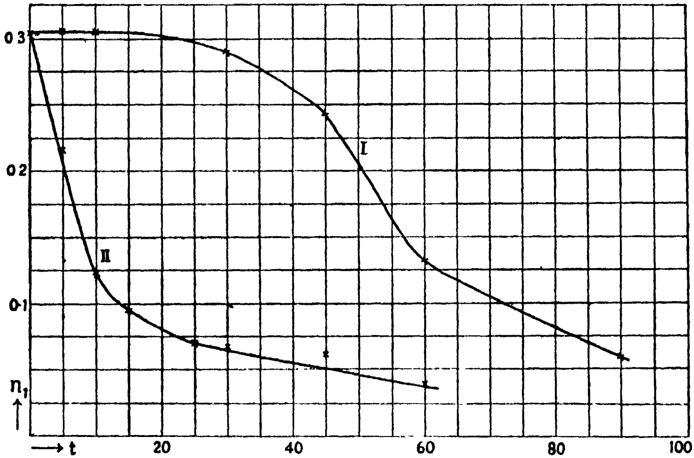

FIG. 21.

addition of electrolytes. In the case of rapid coagulation the values of ζ may be considered to be practically zero, while for slow coagulation the ζ-potential always was found to be below a certain critical value. Therefore every collision is effective throughout the range of rapid coagulation. On the other hand, only a certain fraction of the collisions in the range of slow coagulation are effective because repelling forces due

to the ζ-potential are set up, which prevent close approach of the particles.

The remarkable influence of changes in the concentration of the electrolyte upon the value of ξ and therefore of k_s has been previously noted. This seems to be an outstanding phenomenon, and there appears to be no similar one in all physical chemistry. It is all the more surprising because the rapid rise in the velocity of coagulation with concentration suddenly stops, and the velocity becomes constant as soon as the range of rapid coagulation is reached. The following hypothesis [11] gives a good working basis and seems to go to the very core of the question, although details may have to be changed in many respects.

As was mentioned above only a certain fraction of the collisions are effective in the range of slow coagulation. This may be caused by the fact that the ζ-potential causes forces of repulsion between the particles, and that only when they meet with sufficient momentum do they remain in close contact and coagulate. For the sake of simplicity let us regard the particles, as being of equal magnitude, and let us consider their kinetic velocity as responsible for their coagulation or non-coagulation. Maxwell's curve (Fig. 22) then gives us the distribution of the kinetic velocity for all particles of the sol. Here the abscissæ are the kinetic velocity v, the ordinates the probability w, that the particles have a velocity v. In the range of rapid coagulation the particles are practically uncharged, every collision is effective, and particles having all degrees of energy are coagulated. Their number is

proportional to the total area under the curve. As we approach the range of slow coagulation the electrokinetic potential becomes larger, and every collision is no longer effective because particles meeting with a velocity below a certain critical magnitude are not coagulated. This change is hardly noticeable at first, as long as the majority of particles have a kinetic velocity great enough to cause coagulation. But if the electrokinetic potential becomes still larger, the

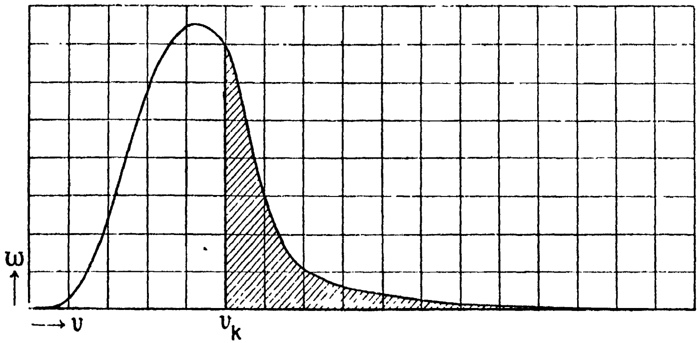

FIG. 22.

critical kinetic energy necessary to cause coagulation is now greater than that possessed by the majority of particles. From this point onwards, as is shown in Fig. 22, the fraction of effective collisions rapidly diminishes and with it the rate of coagulation, because the number of particles having a sufficiently high kinetic energy rapidly grows smaller. If a diagram is drawn in which critical kinetic velocities v_k necessary to cause coagulation are taken as abscissæ, and the number of particles Σn, having this velocity or a

higher one as ordinates, a curve is obtained as shown in Fig. 23. First there is a range of constant value corresponding to the range of rapid coagulation, then a rapid decrease corresponding to the range of slow coagulation.

I may here add parenthetically that I do not feel sure that the velocity of the particles is the variable which is really decisive. It may be that some other

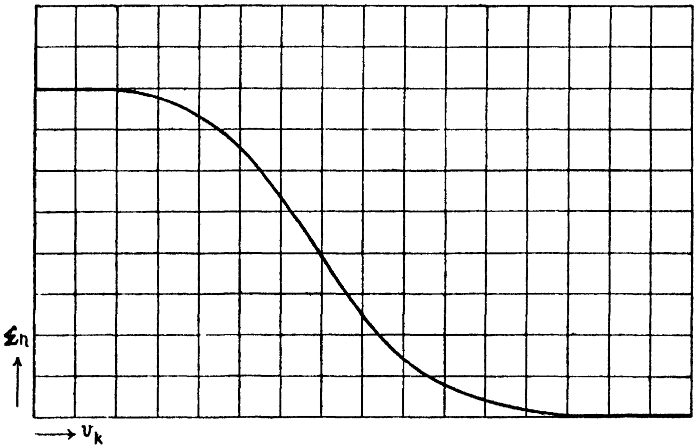

FIG. 23.

quality of the particles, their shape or the distribution of the ions around them, ought to be considered. But I do believe that whatever quality it may be, its distribution over the number of particles will most likely follow Maxwell's law. And the consequences and conclusions will be very much like those drawn here.

If an attempt be made to express these relations in

mathematical form, we may deduce the following equations. The number of particles, whose velocities lie between the kinetic velocities v and $v + dv$, is equal to

$$dn = kv^2e^{-v^2}dv.$$

The number of particles Σn whose kinetic velocities lie between the critical value v_k, necessary for coagulation, and infinity is equal to the integral between this critical velocity as a lower limit and infinity as an upper limit

$$\Sigma n = \int_{v_k}^{\infty} kv^2e^{-v^2}dv = k'\left[v_k e^{-v_k^2} + \frac{1}{2}\sqrt{\pi} - \int_0^{v_k} e^{-v^2}dv\right].$$

This number is proportional to the fraction of effective collisions and therefore proportional to the rate of coagulation :—.

$$k_s = \kappa\left[v_k e^{-v_k^2} + \frac{1}{2}\sqrt{\pi} - \int_0^{v_k} e^{-v^2}dv\right] \quad . \quad (9)$$

It now becomes necessary to develop a correlation between the critical kinetic velocity v_k and the concentration of the electrolyte c. As a first approximation we may consider the critical kinetic velocity proportional to the electrokinetic potential of the double layer of the particles ζ. For ζ we may introduce the following expression :—

$$\zeta = \lambda' \log \frac{g}{c}$$

It was found to hold over a certain range of concentrations, let us say for the initial slope of the curves

in Fig. 15; λ' and g are constants in this equation. Therefore it follows that

$$v_k = \lambda \log \frac{g}{c} \quad . \quad . \quad . \quad (10)$$

It should be noted that these last deductions are a rather weak point in the theory and need a better foundation.

The values of k_s may now be calculated by combining equations (9) and (10).

In the first place it may be shown that the formula fits the limiting conditions. When c is very small v_k becomes large and the integral gives

$$\int_0^\infty e^{-v^2} dv = \frac{1}{2}\sqrt{\pi}$$

so that the second and third terms in the brackets disappear and the first term equals zero. The rate of coagulation k_s is also equal to zero and the sol remains stable. If on the other hand c is large, v_k equals zero, and the first and the third terms of the expression are also equal to zero, k_s is then constant and equal to $\frac{1}{2}\kappa\sqrt{\pi}$. This is the constant value for the rate of rapid coagulation.

Paine and Evans [12] have succeeded in verifying the formula experimentally by using a sol of copper oxide. This is not quite easy because certain difficulties arise if the rates of rapid coagulation and of slow coagulation are to be measured in one series of experiments. For the direct measurement of the rate of rapid coagulation, the concentration of the sol should be very small so

that the time necessary for the change of ν_0 into $\Sigma\nu$ becomes measurable (see equation (2)). In the case of such small concentrations of the sol, it is impossible to measure the rate of slow coagulation with sufficient accuracy under the ultramicroscope. To measure the rate of slow coagulation some indirect methods must be used and these require more concentrated sols. Under such conditions it is impossible to measure the rate of rapid coagulation because the process goes much too rapidly. To avoid this difficulty Paine and Evans used the following device. They added to sols which coagulated too rapidly a small amount of starch. This has a protective action and lowers the rate of coagulation, bringing it again within the realm of measurement. It was found that equal amounts of starch proportionally lower the velocity for different concentrations of electrolyte. In this way Paine and Evans were able to measure coagulation velocities for very low values and thence upwards to the constant rate of rapid coagulation. Their results are given in Table 14.

In this table c is the concentration of the coagulating electrolyte K_2SO_4 in millimoles per liter. k_s is the velocity of coagulation in an arbitrary measure, calculated on the assumption that the sol contained no protective colloid. K_s is the velocity of coagulation, as it was measured. c_s is the concentration of the starch in grams per liter. These measurements agree satisfactorily with the formula as is shown by the following curves (Fig. 24): The abscissæ are log c, the ordinates log k_s. The lines give the theoretical velocity-curves

TABLE 14

c.	k_s.	K_s.	c_s.
0·035	1	1	—
0·047	9·9	9·9	—
0·051	17	0·87	0·0588
0·060	98	4·9	
0·084	1880	4·8	0·0882
0·118	15400	3·2	0·118
0·216	408000	4·2	0·147
0·354	3200000	1·6	0·177
0·414	5400000	2·7	
0·472	9800000	2·9	0·185
0·490	9800000	2·9	
0·826	8800000	2·6	
1·18	8500000	2·5	

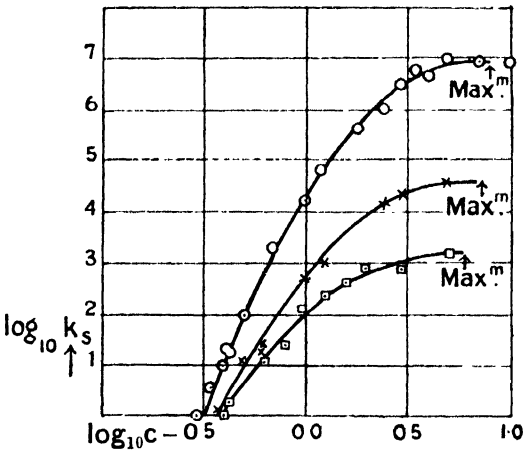

FIG. 24.

according to the formulæ (9) and (10) and the points give the measured values. The three curves refer to measurements with three different sols of copper oxide.

The influence of the temperature is not very different from its influence on rapid coagulation. The factor ξ in equation (8) is not very strongly influenced by temperature and therefore the same terms are subject to its influence as is the case in rapid coagulation. Therefore the expression $k_s = A_s \frac{T}{\eta}$ holds just as in equation (7). The following Table 15, giving the results of measurements with copper oxide sol, shows how well the results agree with the equation.[13] In this table c is the concentration of the coagulating agent Na_2SO_4 in millimoles per liter.

TABLE 15

$c = 0{\cdot}123. \quad A_s = 0{\cdot}000001078$

$t°$.	T.	η.	$\frac{T}{\eta}$.	k_s (obs.).	k_s (calc.).
3	276	0·0161	17140	0·018	0·019
18	291	0·0106	27460	0·030	0·027
37	310	0·00694	44670	0·048	0·051

Finally it may be shown that a coagulation phenomenon of a very different character also displays a behaviour much like the coagulation of dilute hydrophobic sols. If a certain amount of electrolyte such as sodium chloride be added to a concentrated sol of iron oxide, the sols turn into a paste-like gel. By simply shaking this gel it is converted once more into a sol, which may be transformed anew into the gel form.[14] This experiment may be repeated again and again.

The time of transformation is a definite function of the temperature and of the nature and concentration of the electrolyte. The velocity varies with a very high power of this concentration. It behaves in this respect like the rate of slow coagulation. It may then be asked whether it is possible to reach a constant range of rapid coagulation with high concentrations of electrolytes.[15] It is again impossible to measure the rate of rapid coagulation without a suitable modification of method because rapid coagulation proceeds too quickly. For instance, an amount of electrolyte may easily be added so that a person is able to hear the paste change to a fluid when the tube is shaken near the ear. It is impossible to see the transformation because it proceeds too rapidly. Starch has a certain retarding influence, but it is not sufficiently effective. The same holds for other hydrophilic sols. Accidentally it was found that substances like glycine and alanine worked much better. Their influence is not really a protective one, but they seem to raise considerably the electrokinetic potential of the particles, and therefore the velocity of transformation is diminished. The effect of these substances is most likely due to the formation of complex salts upon the surfaces of the particles. If a sol containing a certain amount of glycine is used and an electrolyte is added in increasing concentration, the same behaviour is found as in the case of the coagulation of dilute hydrophobic sols. At first there is a rise in the velocity throughout the range of slow coagulation; then a constant value for the range of rapid coagulation. Expression (8) holds again, pro-

vided that a different relation is used between the value v_k and the concentration of the electrolyte c. The simple formula

$$v_k = \lambda - gc \quad . \quad . \quad . \quad (11)$$

agrees better with the measured values. Fig. 25 shows how well the values of k_s, calculated by equations (9) and (11), agree with the measured values. The calculated values are given again by the curve drawn in

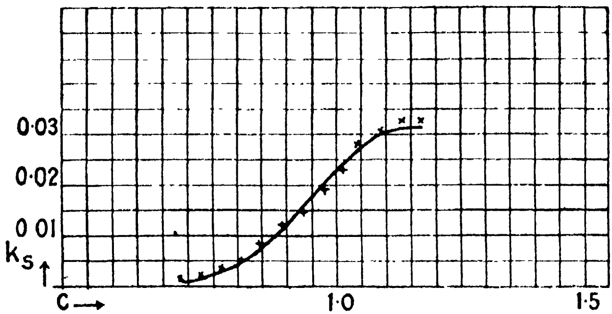

FIG. 25.

full, the observed values by the points. The abscissæ are the concentrations of the coagulating agent KCl in moles per liter, the ordinates the value of k_s.

This change of a sol into a gel and of a gel into a sol by such a simple mechanical influence as shaking, is a phenomenon of biological importance. We know cases in which the protoplasm behaves in very much the same way. These experiments therefore have not only theoretical interest, but they may have a still broader application.

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CHAPTER V

THE STABILITY OF HYDROPHILIC SOLS

INVESTIGATORS hold rather diverse opinions about the causes of the stability of hydrophilic sols. Nevertheless the conceptions developed by Kruyt and his co-workers [1] seem to me to be so important that it may be worth while to discuss them, although many other workers in the field of colloidal chemistry have not accepted them.

The principal ideas of Kruyt are as follows: The stability of hydrophobic sols is due chiefly to one factor, the electrokinetic potential of the colloidal particles. This factor is also of influence in hydrophilic sols, but a further factor is present which is the hydration of the colloidal particles. Hydration in hydrophilic sols plays a rôle similar to hydration in true solutions. Molecules of the dissolved substance which are highly hydrated are more soluble in water than molecules of a substance which is less hydrated. This greater solubility in true solution corresponds to a greater stability of a sol in the field of colloids.

Kruyt has developed methods which enable him to distinguish between these different factors of stability, i.e. the electric factor and the hydration factor. He

made use of an agar sol in his studies. This may be regarded as typical of hydrophilic sols, since it is indifferent to the addition of low concentrations of electrolyte, is only salted out by some electrolytes at high concentrations, is able to form a gel, and does not show discrete particles under the ultramicroscope. It might be doubted whether the stability of the sol would be influenced at all by an electrokinetic factor, but the following experiment shows this to be the case. Kruyt measured the viscosity of a well-dialyzed agar sol above 40°. At this temperature it shows no tendency to form a gel and follows Poiseuille's law. If small amounts of electrolyte are added, the viscosity is lower, but it soon reaches a practically constant value for the higher concentrations of added electrolyte. This lowering of the viscosity depends mainly on the valency of the cation, univalent ions being of much smaller influence than bi-, tri- and quadrivalent ions. Fig. 26 shows this clearly. The abscissæ are the concentrations of electrolytes, the ordinates the relative changes of viscosity $\frac{\eta_s - \eta_m}{\eta_m}$. Here η_s is the viscosity of the sol containing the electrolyte, η_m the viscosity of water. Curve I refers to KCl, II to $BaCl_2$, III to $[Co(NH_3)_6]Cl_3$ and IV to $[Pt(NH_2.CH_2.CH_2.NH_2)_3](NO_3)_4$.

Such a distinct influence of valency always points towards some electrokinetic influence. Kruyt explained it in the following way. According to Smoluchowski[2] the electric charge of colloidal particles increases the viscosity of the sol. He developed an equation

$$\eta_s = \eta_m \left\{ 1 + 2 \cdot 5 \phi \left[1 + \frac{1}{\lambda \eta_m r^2} \left(\frac{D\zeta}{2\pi} \right)^2 \right] \right\}$$

or

$$\frac{\eta_s - \eta_m}{\eta_m} = 2 \cdot 5 \phi \left[1 + \frac{1}{\lambda \eta_m r^2} \left(\frac{D\zeta}{2\pi} \right)^2 \right].$$

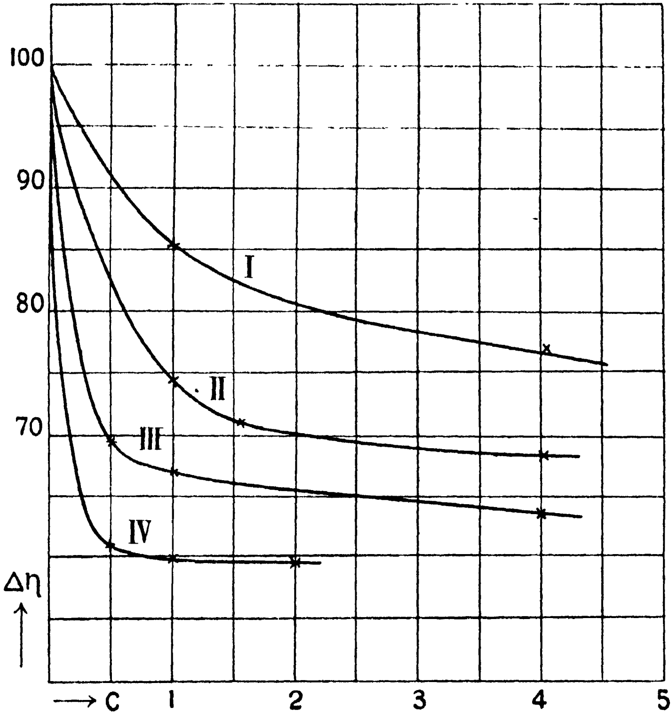

FIG. 26.

Here η_s is the viscosity of the sol, η_m that of water, ϕ is the specific volume of the colloidal particles, r their radius, λ the conductivity of the sol, D the dielectric constant, and ζ the electrokinetic potential.

By adding electrolytes the ζ-potential is made to disappear and the second expression in the brackets, which is always positive, becomes zero. We then obtain a smaller value for the viscosity of the sol,

$$\frac{\eta_s - \eta_m}{\eta_m} = 2{\cdot}5\phi.$$

This is the formula for the viscosity of a sol given by Einstein in which no account is taken of any electrically charged particles. Since the ζ-potential is mainly influenced by the valency of the ions of opposite charge, we must expect a similar effect upon the viscosity of the sol, provided that the particles of the sol have a ζ-potential.

In a hydrophobic sol the addition of electrolytes and the lowering of the ζ-potential, which is correlated with it, would cause the coagulation of the sol. In an agar sol such a coagulation does not take place because the hydration of the particles keeps them in colloidal solution although they have lost their electric charge. If then we succeed in dehydrating the particles of the sol, the stability of the sol is diminished so much that it is coagulated.

Kruyt found two methods for the dehydration of the colloidal particles. The first method consisted in adding to the sol substances which are themselves strongly hydrated. These substances tend to deprive the particles of their water molecules. Typical materials of this class are alcohol and acetone. If they are added to an agar sol containing small amounts of electrolyte, the sol is coagulated. Here the only

factor causing stability, the hydration of the particles, is destroyed. If alcohol is added to this agar sol without having added any electrolyte, the sol still shows a certain stability, because the particles retain their electrokinetic potential. But the sol is changed so to speak into a hydrophobic sol. It is now very sensitive to electrolytes and is coagulated by them according to the valency rule. Table 16 contains some coagulation values γ in millimoles per liter (see p. 42) for an agar sol containing alcohol. The particles are now easily seen under the ultramicroscope, because they are no longer strongly hydrated, and their refractive index is therefore sufficiently distinct from that of the surrounding medium.

TABLE 16

Electrolyte.	γ (Millimoles per liter).
KCl	14
$BaCl_2$	0·53
$[Co(NH_3)_6]Cl_3$	0·33

Similar changes can be produced in the agar sol by a substance of a very different kind. Small amounts of tannin coagulate the agar sol, provided this contains sufficient amounts of electrolytes to make the ζ-potential zero. If the tannin is added to the sol, before the addition of the electrolytes, the sol retains a certain stability, but it is changed into a more hydrophobic sol. It is sensitive to electrolytes in small concentrations, being coagulated according to the valency rule (Table 17). The liquid is opalescent or even milky, and the particles are again visible under the ultramicroscope.

TABLE 17

Electrolyte.	γ (Millimoles per liter).
KCl	12
$BaCl_2$	1·9
$[Co(NH_3)_6]Cl_3$	0·14

There is a distinct difference between the behaviour of such substances like alcohol or acetone on the one hand and tannin on the other. It is necessary to add rather large amounts of alcohol, up to 40 per cent. and more, to cause dehydration, whereas tannin shows its influence most strongly in low concentrations. In the case of the alcohol we distinctly have an influence of mass-action. The influence of the tannin is explained by Kruyt and Bungenberg de Jong in the following way. It is very probable that the tannin is adsorbed by the agar particles. This explains why its influence is strongest in small concentrations. Furthermore, tannin has a distinctly polar structure. Its formula is $C_6H_7O_6[C_6H_2(OH)_3COOC_6H_2(OH)_2CO]_5$. The aromatic digalloyl groups are rather hydrophobic, the glucose group is hydrophilic. Kruyt and Bungenberg de Jong make assumptions similar to those which were made by Langmuir [3] and Harkins [4] in order to explain the behaviour of oil-films on water-surfaces. The latter assume that, for instance, the molecules of the fatty acids are orientated, the hydrophilic COOH-group being turned towards the water-surface, the hydrophobic CH_3-group towards the gas-phase. Kruyt and Bungenberg de Jong believe that the molecules of tannin are orientated on the surface of the agar particles in such a way that the glucose group lies next to the

agar surface while the aromatic groups project into the liquid phase. As a result the particles are now covered with a hydrophobic surface. If this is true, it might be asked whether the influence of the tannin is really a dehydration of the particles or rather a transformation of their surface only into a more dehydrated state.

The difference between the behaviour of alcohol and tannin is also shown by their influence on the viscosity of the agar sol. Fig. 27 gives the curve showing the influence of alcohol. The abscissæ are concentrations, the ordinates the values $\Delta\eta = \frac{\eta_{s+a} - \eta_{w+a}}{\eta_{w+a}}$ where η_{s+a} is the viscosity of the agar sol containing alcohol and η_{w+a} the viscosity of the solutions of alcohol and water. Fig. 28 gives a similar curve for tannin. Here the abscissæ are percentage concentrations of tannin, the ordinates the values $\Delta\eta = \frac{\eta_{s+t} - \eta_{w+t}}{\eta_{w+t}}$ where η_{s+t} is the viscosity of the sol containing tannin and η_{w+t} the viscosity of the tannin solution. A hydrophilic sol has generally a much higher viscosity than a hydrophobic sol. Dehydration therefore shows itself by a marked decrease of viscosity. In the case of the alcohol, this distinct decrease begins at a concentration of about 40 per cent., whereas with tannin the decrease of viscosity is greatest at the lowest concentrations.[5]

The agar sol containing tannin may be rehydrated and so transformed again into a hydrophilic sol. This rehydration is also in full agreement with the theory just developed. Rehydration may be produced by

increasing the temperature. The sol becomes less opalescent and looses its sensitiveness towards electrolytes. This influence of temperature is due to the fact that the adsorption of tannin is lowered by increasing

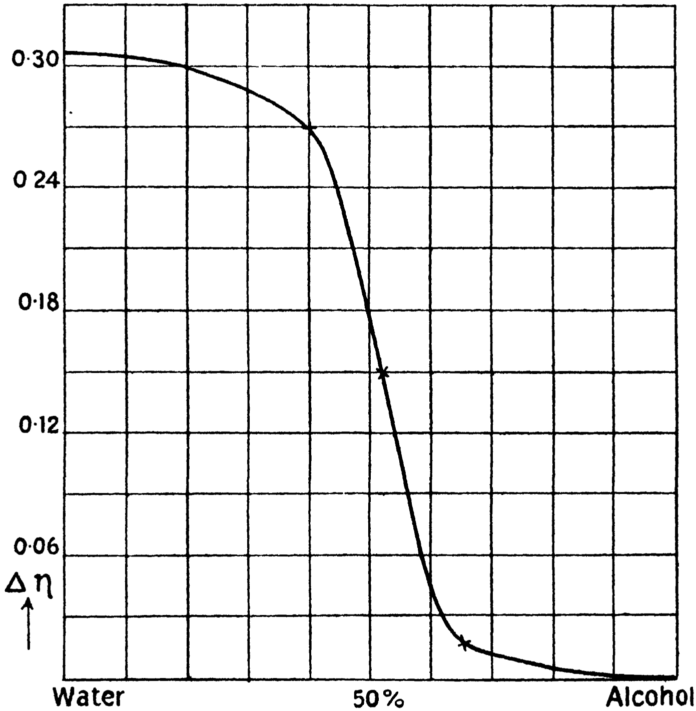

FIG. 27.

the temperature. Rehydration may also be effected by adding substances like glycol or glycerine. They most likely change the character of the medium in such a manner that the tannin is adsorbed less strongly by the particles. The addition of substances like

alcohol produces a rather complicated result which, nevertheless, may be explained from the standpoint of this theory. Low concentrations cause rehydration because they act in a manner similar to glycol or glycerine. The agar-tannin sol therefore becomes more

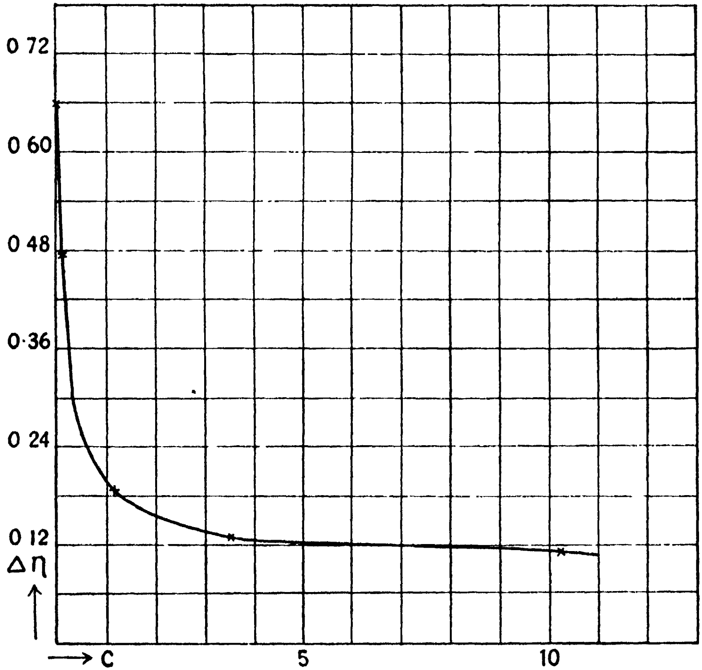

FIG. 28.

hydrophilic. At high concentrations, on the other hand, the above-mentioned dehydrating effect of alcohol makes itself felt. The sol returns again into a more hydrophobic state. Alkali also causes a rehydration of an agar-tannin sol, most likely because it

forms salts with the tannic acid and these do not have the dehydrating effect of tannin.

The stability of an agar sol can be represented symbolically in the following way (Fig. 29): + and — show the existence of a ζ-potential, the circle around the particle is used to designate the hydration.

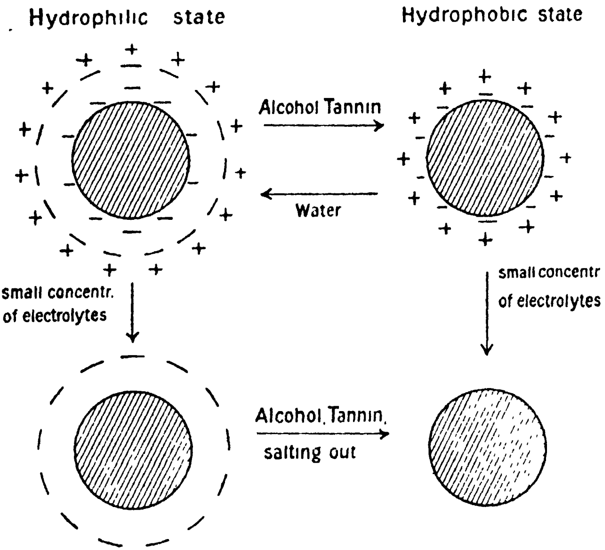

FIG. 29.

In the original hydrophilic state both stabilizing factors exist. Fig. 29 shows how the one or the other may be destroyed by the addition of small amounts of electrolytes or of substances like alcohol, tannin, etc.

The salting out effect of electrolytes in high concentrations may also be understood from the standpoint of this theory. In high concentrations electrolytes,

which are themselves strongly hydrated, may dehydrate the agar particles just as the particles are dehydrated by alcohol. Since the electrolytes in low concentrations already have destroyed the stabilizing factor, due to the electric charge, the sol coagulates at higher concentrations because the particles are now dehydrated. This dehydrating effect makes itself evident in a de-

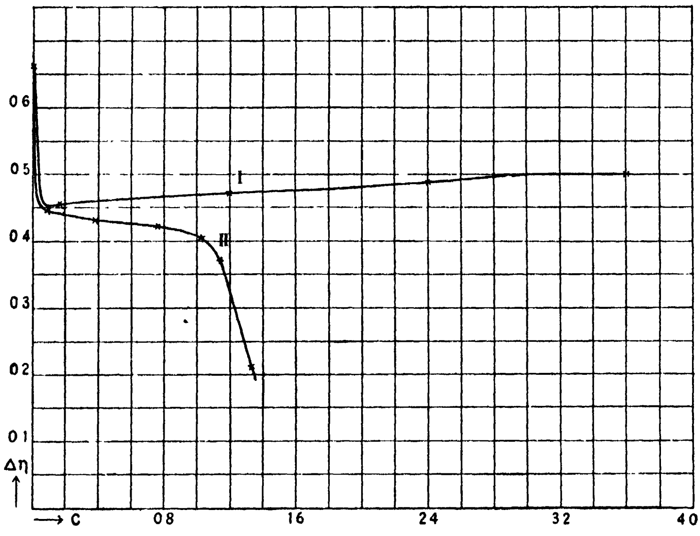

FIG. 30.

crease of the viscosity. In Fig. 30 the abscissæ are concentrations of electrolytes in equivalents, the ordinates the values $\Delta\eta = \frac{\eta_{s+e} - \eta_{w+e}}{\eta_{w+e}}$. Here η_{s+e} is the viscosity of a sol containing electrolytes and η_{w+e} the viscosity of the aqueous solution of the electrolyte. A salt like $MgCl_2$ which shows no salting out effect

only causes a certain decrease of viscosity at very low concentrations. This results from a discharging of the particles. $MgSO_4$, on the other hand, a salt which has a salting out effect, not only shows this initial decrease, but an additional large decrease at higher concentrations. This may be correlated with the dehydrating effect of the salt.

How far these results may be generalized and applied to other sols remains to be seen. According to Bungenberg de Jong, the behaviour of protein sols towards tannin is fully in accord with this theory. He investigated especially the effect of tannin and other tanning substances upon gelatine solution. The conditions are much more complex because of the amphoteric character of the proteins. This makes it necessary to extend the symbolic diagram given above (Fig. 29) in the following way (Fig. 31): Nos. 1 to 5 illustrate the protein particle in its hydrated form. In No. 3 it is at the so-called isoelectric point, its ζ-potential being zero. Small concentrations of $H^{\cdot}$-ion cause a positive charge, represented by No. 2. Still higher concentrations of $H^{\cdot}$-ion allow this positive ζ-potential to disappear again as indicated by No. 1. In a similar way, small concentrations of OH'-ion produce a negative charge as shown by No. 4, and this disappears again at a higher concentration as illustrated by No. 5. Dehydrating influences like alcohol or tannin destroy the stability factor caused by the hydration and this state of the particle is represented by Nos. 6 to 10. In cases numbered 6, 8, and 10 no stability factor remains and we have coagulation. In cases numbered 7 and 9 the

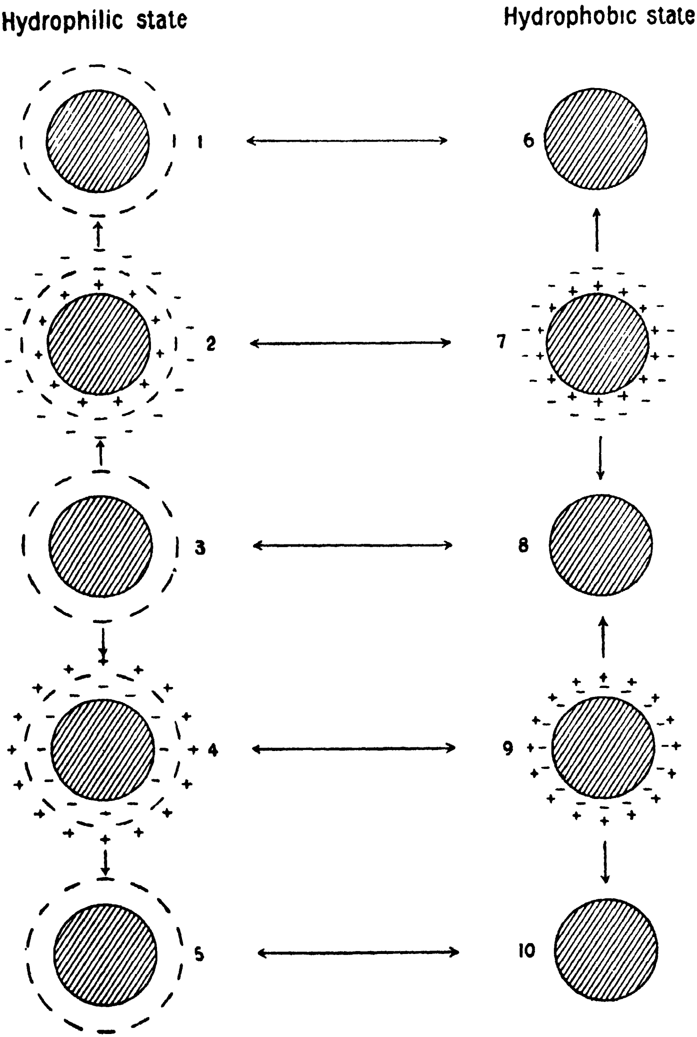

FIG. 31.

ζ-potential causes a certain stability and the protein sols ought to behave in these cases like a hydrophobic sol. According to Bungenberg de Jong the behaviour of gelatine solution towards tannin is indeed markedly in agreement with this diagram. But the great instability of gelatine in water solution, especially at higher temperatures, does not allow the testing of many points of this theory. Experiments by Lier with a casein sol also proved the existence of two influences responsible for the stability of hydrophilic sols. Small concentrations of electrolytes destroyed the electroviscous effect, in accordance with the charge of the particles and the valency rule. Substances like alcohol and acetone acted as dehydrating agents.

The investigation of a system not belonging strictly to one or the other class of any classification, but having properties midway between is often very valuable in clearing up theoretical questions. Systems of this type, which are applicable in this case, are the sols of sulphur, which may be prepared by the interaction of SO_2 and H_2S or by the decomposition of $Na_2S_2O_3$ with acids. These sols are often called Odén's [6] sulphur sols. They behave on the whole as hydrophobic sols, being sensitive towards small concentrations of bi- and trivalent cations, and their particles are easily seen under the ultramicroscope. But these sols have some properties which distinctly remind one of hydrophilic sols. They are very easily peptized and are extraordinarily stable towards $H^{\cdot}$-ion and univalent cations. This behaviour is especially striking if it is compared with the stability of a sulphur sol prepared

according to a method of v. Weimarn,[7] by pouring an alcoholic solution of sulphur into water and evaporating the alcohol. This Weimarn sol behaves exactly like any hydrophobic sol. It is sensitive towards small concentrations even of univalent cations and still more sensitive towards $H^{\cdot}$-ion. In the following table (Table 18) the behaviour of these two sols is compared. The γ values are coagulation values (see p. 42) in millimoles per liter.

TABLE 18

Electrolyte.	γ of Weimarn's sulphur sol.	γ of Odén's sulphur sol.
LiCl	34	640
NaCl	34	220
KCl	32	95
RbCl	31	80
CsCl	30	95
HCl	10	650
NH_4OH	About 5000	—
$CaCl_2$	3·8	1·6
$CeCl_3$	0·2	0·05

The stability of Odén's sols may be explained in the same manner as Kruyt explained the stability of hydrophilic sols.[8] There is an electric factor responsible for the stability and, in addition to this, a factor of hydration. The hydration is caused by the presence of a special substance which is contained in Odén's sol but not in the Weimarn sol. This substance is pentathionic acid, $H_2S_5O_6$. It is very stable in aqueous solution as long as the solution is acid. It may bring about the

hydration of the sulphur particles in a manner similar to the production of a hydrophobic surface in an agar sol by tannin. The large number of O-atoms in the pentathionic acid have a distinct affinity for the water molecules, whereas the sulphur atoms tend to be attracted towards the elementary sulphur. This may be assumed since sulphur has such a strong tendency to form polyatomic molecules. Pentathionic acid might therefore well be able to link the water molecules with the sulphur particles.

All factors which increase the stability of the pentathionic acid will also stabilize Odén's sulphur sols. This explains why the sol is not very sensitive to acids. Univalent cations will also have a certain stabilizing effect, because they may introduce a certain number of water molecules according to their degree of hydration. The fact that the strongly hydrated Li-ion has but a weak coagulating action agrees well with this assumption. We also find the so-called Hofmeister series in the coagulation values of the alkali metals. The amount of hydration changes in accordance with this series.

On the other hand, all factors which decompose pentathionic acid will decrease the stability of Odén's sol because they destroy the hydration factor and transform the sol, so to speak, into a hydrophobic Weimarn sol. This sol is much less stable. Pentathionic acid is easily decomposed by alkali. Accordingly OH'-ion has a marked influence on Odén's sol. It changes its colour from yellow to white and coagulates it, although the negative ζ-potential of the

sulphur particles is increased by small concentrations of OH′-ion. High concentrations of H_2S are also able to decompose pentathionic acid, and again it is found that Odén's sol may be coagulated by treating it with high concentrations of H_2S.

The above explanation receives additional weight when it is found that sulphur sols similar to Odén's are formed when sulphur is precipitated in a finely divided state in the presence of pentathionic acid. The decomposition of S_2Cl_2 by water according to the equation

$$5S_2Cl_2 + 6H_2O = 5S + H_2S_5O_6 + 10HCl$$

is just such a reaction. The sol which is formed contains pentathionic acid and has the same properties as Odén's sulphur sol.

Thus the behaviour of sulphur sols is in complete agreement with Kruyt's theory. This means that we are able to distinguish two different factors of stability: an electric factor and a factor of hydration.

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5. The influence of the tannin on viscosity is not like the influence of electrolytes on the viscosity, as it is not due to a lowering of the ζ-potential. This is shown by the following facts. The agar-tannin sol has the same ζ-potential as the original agar sol. The stability of the agar-tannin sol is only due to its electric charge. It acts like a hydrophobic sol, whereas an agar sol, containing a small amount of electrolyte, shows a stability caused by hydration, behaving like a hydrophilic sol.

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CHAPTER VI

THE STATE OF AGGREGATION AND THE SHAPE OF COLLOIDAL PARTICLES

UNTIL recently the state of aggregation and the shape of colloidal particles received but little attention from investigators. It was felt by some that the particles were amorphous and consequently spherical, and by others that all sols contained particles of crystalline structure. Only a few isolated observations of a specific character had been made, such as those of Zsigmondy and Bachmann [1] who found thread-like particles in soap solutions. Furthermore it was known that iron oxide sols exhibited the so-called Majorana-phenomenon,[2] that is, they showed double refraction when subjected to the influence of a magnetic field. This was explained by assuming a definite structure of the particles and a consequent orientation in the magnetic field. This explanation could not be confirmed by ultramicroscope observation. During the last ten years, however, our knowledge of the state of aggregation and the shape of colloidal particles has developed rapidly, and it will be the purpose of this chapter to outline our present state of information in this field.

The method of X-ray analysis, as developed by Debye and Scherrer [3] and also by Hull,[4] enables one to decide between the amorphous and crystalline state of the colloidal particles. Monochromatic X-rays are allowed to enter a lead chamber and pass through a rod of the finely divided solid. This consists of the particles of the sol which have been separated from the liquid by ultrafiltration. A more direct method of investigation has been used whereby a small jet of the sol was allowed to flow through the lead chamber in a position similar to that of the small rod of particles.[5] The sol must be sufficiently concentrated in order to produce an X-ray diagram. The jet or rod is surrounded by a photographic film. If the substance is crystalline, sharp lines will appear on the developed film. On the other hand, a uniform darkening or broad bands will result if the substance is amorphous.

In this way it was found that the particles of very many sols are crystalline. The particles of gold and silver sols which were investigated by the jet method gave the same X-ray diagram as the massive metals. The particles of Al_2O_3- and Fe_2O_3-sols also showed a crystalline structure.[6] A definite tendency to remain amorphous was found for the particles of CeO_2-, ZrO_2, and ThO_2-sols. Haber [7] has pointed out that the factors influencing the velocity of the formation of the particles are decisive for their state of aggregation. There appears to be a competition between a *grouping velocity* and an *orientation velocity*. If the period of precipitate formation is very short, a sufficient time does not elapse for a definite orientation of the molecules to take place.

The particles remain in a state of disorder and the precipitate is amorphous. This is true for the precipitation of $Al(OH)_3$ and $Fe(OH)_3$ when the precipitates are rapidly formed from solutions by alkalies. If on the other hand there is a longer time of formation, as in the case when aluminium oxide or iron oxide sols are formed by hydrolysis, the process of orientation takes place and the particles are crystalline. This is only true when the tendency for crystal formation is sufficiently great. In many sols, as for example those of CeO_2-, ZrO_2-, and ThO_2-, this tendency is present to such small extent that the particles of the freshly-prepared sols are amorphous and become crystalline only after a long period of time.

I should like to remark here that I believe the two states of aggregation mentioned, the crystalline and the amorphous-solid states, are not the only ones that we are obliged to distinguish. It seems to be very likely that the particles of quite a number of sols, for instance of soap solutions, of lecithin sols and others are in a mesomorphous condition, that is to say, they are in a state of aggregation known as crystalline liquid. This is a question which will be discussed later.

If the particles of a sol are amorphous, their shape will as a rule be spherical. This seems to hold for the particles of CeO_2-, ZrO_2-, ThO_2-sols and others because their particles are amorphous and show no phenomena characteristic of non-spherical particles. But we have important and rather surprising exceptions which will be considered at the end of this chapter.

The manifold phenomena which are caused by the

non-spherical shape of the particles will first be discussed. If they are visible in the ultramicroscope they exhibit pronounced *scintillation* and not a continuous radiation of light as in the case of a sol with spherical particles. The cause of this scintillation has been determined by Siedentopf [8] in his researches with the microscope, and the same consideration may be applied to the behaviour of the particles in the ultramicroscope. An elongated particle can be seen in the ultramicroscope only when the light rays strike the particle perpendicularly to its longitudinal axis and when the particle lies in the plane of observation of the microscope. As a rule, if the light strikes the particle in a direction parallel to its longitudinal axis or if the particle is perpendicular to the plane of observation, it cannot be seen. Since the particles have a Brownian movement they become luminous when in the correct position and disappear in all other positions. This gives rise to scintillations.

It is possible to intensify this effect by using the cardioid ultramicroscope with certain diaphragms such as the azimuth and aperture diaphragm. Siedentopf [9] already has used the azimuth diaphragm in researches with the microscope. Szegvari [10] was the first to introduce it for ultramicroscopic investigations. The applicability of the azimuth diaphragm depends upon the phenomenon just mentioned, that elongated particles are visible in the ultramicroscope when the light strikes them perpendicularly to their longitudinal axis and when they lie in the plane of observation. In the slit ultramicroscope, the light always enters in a definite

direction and it cannot be changed at will. In the cardioid ultramicroscope, on the other hand, this may be done. In this instrument the light rays enter the cell from all sides. If an azimuth diaphragm, that is a movable slit diaphragm is introduced under the condenser, then by turning the diaphragm, the light can be made to strike the ultramicroscopic preparation from any desired direction. Although the details will not be discussed here, Szegvari has shown that in the use of the azimuth diaphragm a suitable aperture must be employed. He therefore always uses the azimuth diaphragm together with a suitable aperture diaphragm, an iris diaphragm, which enables him to obtain the correct setting of the aperture.

If these diaphragms are used for a sol with rod-like particles then the scintillations are distinctly more intense than those observed in the slit ultramicroscope. This is caused by the fact that the optical conditions are better suited for the observation of the scintillation. If we use a gel we observe no scintillations because the particles do not move, but they are only visible when the light strikes them in the proper direction.

The sol with non-spherical particles, whose properties have been studied most extensively, is the sol of V_2O_5.[11] It is easily prepared as follows.[12] Ammonium vanadate is ground up with dilute hydrochloric acid, and the flocculent precipitate of V_2O_5 which forms is removed from the liquid by filtration and washed with water until it begins to pass through the filter. The precipitate is then removed from the filter and dispersed by shaking it vigorously with a suitable quantity of

water. The sol is a clear liquid of a beautiful reddish-brown colour. When freshly prepared it gives, as a rule, no indications that the colloidal particles are non-spherical. It is only after the sol has aged that the properties, which are due to a definite structure of the particles, become more and more evident. Under proper conditions a sol, which has aged, shows rod-like particles, possessing a slow Brownian movement which can be observed with the ultramicroscope. Longitudinally the particles are of microscopic dimensions, often more than 1μ, but their lateral dimensions remain ultramicroscopic, or amicronic, and therefore the particles cannot be seen in the microscope. If the particles are smaller than those mentioned, they only show very pronounced scintillations if the azimuth diaphragm is used.

The particles of the sol are unquestionably crystalline. They give distinct lines when analysed by the X-ray method. Fig. 32 was obtained by Laue's method, using a film of the particles made in the following manner. A concentrated sol was allowed to flow down a glass plate. The movement of the liquid caused the rod-like particles to assume a direction practically parallel to the lines of flow. This will be discussed more fully later on. The water was then evaporated and this process repeated several times until the deposit of particles became sufficiently thick. We have a fibrous structure like that of threads of cellulose, and the diagram shows the characteristic picture of the fibrous structure with symmetrical dark spots.[13]

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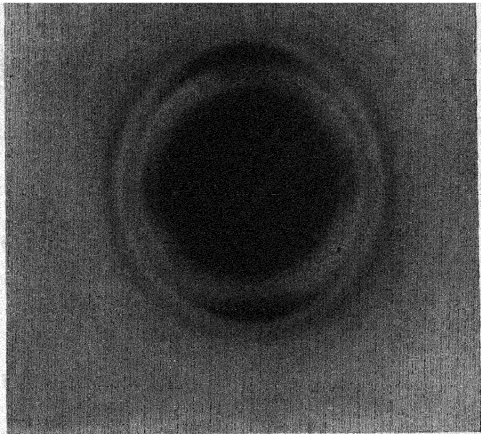

FIG. 32.

FIG. 33.

FIG. 34.
Direction of the Azimuth diaphragm —

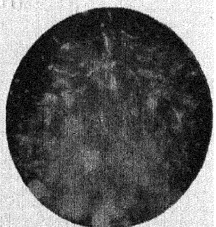

FIG. 35.
Direction of the Azimuth diaphragm |

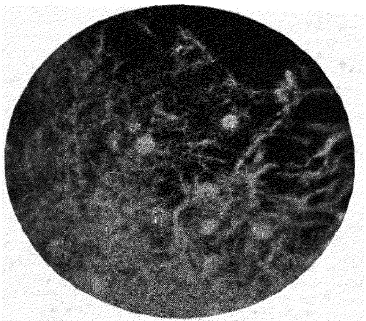

FIG. 36.

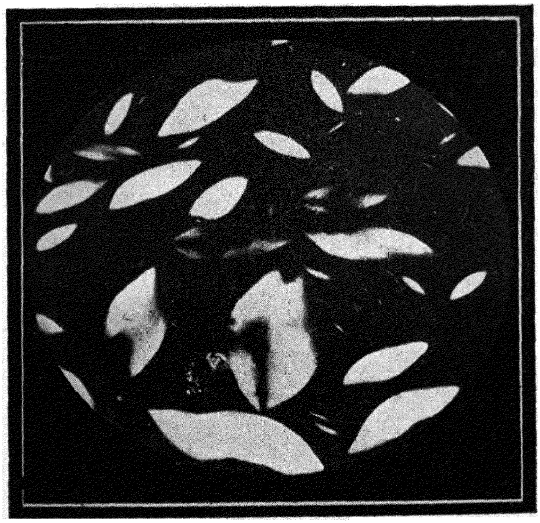

FIG. 37.

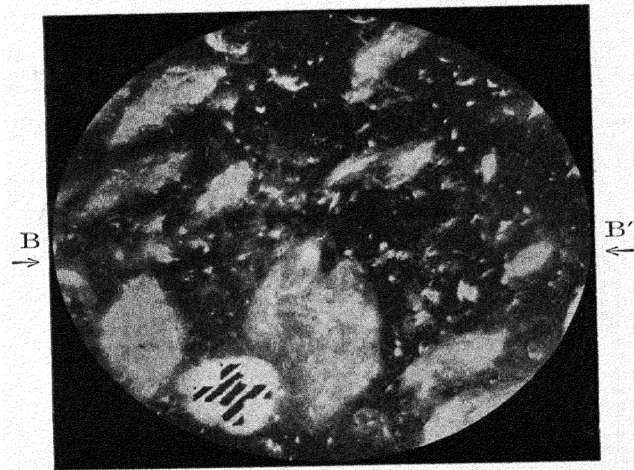

FIG. 38.

It has also been observed that the particles of old and concentrated V_2O_5-sols have arranged themselves more or less regularly in *cloud-like swarms.* The subjoined photographs (Figs. 33-35) taken by Szegvari [10] give a picture of one and the same spot in a colloidal solution of V_2O_5 photographed, first in Fig. 33, without an azimuth diaphragm, then two cases (Figs. 34 and 35) in which it is used. In Fig. 34 the slit of the diaphragm was used perpendicularly to the case given in Fig. 35. It must be emphasized here that the sol as examined in these pictures was not coagulated. A coagulated sol gives an entirely different picture (Fig. 36).

The particles cause double refraction when orientated in a definite direction because the crystalline particles themselves cause double refraction. Since they are orientated parallel to one another in these cloud-like clusters they are in a proper position to show double refraction. Bright patches are therefore visible when a thin film of V_2O_5-sol is viewed between crossed Nicol prisms in a polarizing microscope.

The older and the more concentrated the sols become the more pronounced are these swarms and clusters, as Zocher [14] was the first to show. In the lower layers of such sols there may be found drops of fluid which give in the polarizing microscope, between crossed Nicol prisms, a picture such as Fig. 37. Flamelike clusters are to be seen. Under the cardioid ultramicroscope with an azimuth diaphragm these clusters are found to consist of long thread-like particles arranged parallel to one another, showing weak scintillation caused by the Brownian movement within the cluster (Fig. 38).

These clusters are not yet crystals. If the liquid is shaken up or mixed thoroughly by moving the glasses, which hold it under the microscope, over one another, the clusters disappear and the double refraction of the layer becomes practically homogeneous. But after a certain lapse of time they are formed again.

Zocher found that some old and concentrated sols of iron oxide show this phenomenon in a more pronounced and somewhat surprising form. The V_2O_5-sol only contains particles with a longitudinal axis, in other words they are rod or threadlike. Iron-oxide sols on the other hand contain particles which have the form of lamellæ. These particles of iron-oxide sols [15] may settle in absolutely regular layers, parallel to the bottom of the flask or of the object glass. The distance between two layers is so regular that a beautiful iridescent green colour is caused by the interference of the light reflected from these layers. Since the iridescence of the scales of many butterfly wings is caused by the interference of light reflected or refracted by parallel layers of chitin,[16] it is evident that the colour of these layers of iron oxide looks just like the iridescent colour of butterfly wings. This phenomenon is also reversible. If the fluid is shaken or the layer destroyed by moving the object- and cover-glasses against one another, these layers and with them the iridescent colour, disappear. But they are formed again in a few days. The colour is a green of the second order and the distance between two layers may be calculated as about $1/4\mu$.

With an ultramicroscope using the azimuth dia-

phragm these layers may be seen directly. The particles constituting them are not absolutely motionless, but they show weak scintillation as a result of their Brownian movement. Under the influence of electro-endosmosis with the electric current passing through these layers parallel to their planes, the fluid is pressed out and the layers approach each other. The colour of iridescence changes from the green of the second order to red of the first order. If small amounts of electrolyte are added carefully a coagulation takes place. The regular position of the layer is destroyed and the iridescent colour becomes irregular and passes through the blue and violet of the second order and the red, yellow, and green of the first order until it reaches the bluish-green of the first order.

These facts enable us to understand how such layers are formed. We arrive according to Haber [17] at the best explanation for this phenomenon if we consider the behaviour as due to the electrical double layer which we have discussed in the preceding chapters. The electrical double layer on the surface of colloidal particles extends rather deeply into the liquid phase. The particles behave as if envelopes of ions are around them. If the particles are brought nearer to one another, these envelopes are distorted and this causes attracting and repelling forces between them which may lead to a state of equilibrium such as is shown by these layers. The attracting forces result from an electrical attraction caused by an asymmetrical position of the ions towards the particles. The repelling forces may result from osmotic influences, the ions trying to

recover their former regular position around the particles. Since these envelopes extend rather deeply into the interior of the liquid, such states of equilibrium may exist even when the particles are rather far apart. By adding electrolyte the fall of potential on the surface of a particle becomes decidedly greater and the extension of the ionic envelope into the interior of the liquid is very much reduced. The particles approach each other more closely before the ionic envelopes are able to assert their influence. This is the case of coagulation, which was considered in preceding chapters. The rather extraordinary form of these structures in the V_2O_5- and especially in the iron-oxide sols are caused by the fact that the particles of the sol have a very specific shape.

The existence of such sol structures and the significance of the ionic envelopes, referred to in this and in the preceding chapters, show that in sols with little electrolyte and not too dilute, the particles are subject to much greater mutual forces, and are therefore much less independent of one another than was formerly supposed to be the case. It is only at larger contents of electrolytes that the particles move in virtual independence of one another, provided the distance between them is sufficiently great.

Mention has been made of the phenomenon of the *double refraction* which is shown by these sols and is due to small crystals which are double refracting. If they are arranged in a regular way, as is the case in these swarms, the double refraction becomes noticeable. In dilute sols this is as a rule not the case. The par-

ticles move about under the influence of the Brownian movement in complete disorder and the influence of one particle on double refraction is neutralized by the influence of another particle having a different position. But the double refraction can be made visible by arranging the particles in a regular order. This can be attained by various methods, such as the influence of a magnetic field, the influence of an electrical current, or simply, as was mentioned before, by causing the liquid to flow in a regular way.[18] If for instance the V_2O_5-sol is allowed to flow through a tube with parallel walls, it exhibits double refraction similarly to the lamellæ of a uniaxial crystal, which has been cut parallel to its axis and whose axis lies in the direction of flow. A strong illumination is observed through crossed Nicol prisms if the electrical vector of the illuminating ray is inclined at an angle of 45° to the perpendicular direction of flow.

In the case of V_2O_5-sol, in contrast to the Fe_2O_3-sol, the particles are often large enough to be seen under the ultramicroscope, and it can be directly determined whether or no the particles are orientated in the manner assumed above.[19] In accordance with the above-mentioned optical behaviour, which gives rise to scintillations, only those particles can be seen in the slit-ultramicroscope which lie approximately perpendicular to the illuminating rays in the plane of observation. If an electric current is passed through the sol in the ultramicroscope in a direction parallel to that of the light rays, then the particles disappear and the observation field becomes dark. The particles

now lie with their axes parallel to the direction of the current and the light rays strike the particles parallel to their axes. If the electric circuit is opened, then the Brownian movement causes the particles to assume their original state in a minute or so.

The same experiments may be repeated with an iron-oxide sol.[18] Not only is the sol doubly refracting under the influence of a magnetic field, and under the influence of an electric field, but also when subjected to flow. This shows that the Majorana phenomenon mentioned above is but a special case of a more general group of phenomena, which are observed with sols containing non-spherical particles, when these are subjected to influences that effect a definite orientation of the particles. These particles of an iron-oxide sol cannot be seen with the ultramicroscope. But Szegvari [10] was able to make their scintillation visible by using the azimuth diaphragm. This shows that the particles are not spherical. They seem to be lamellæ, as mentioned above, according to some experiments by Diesselhorst and Freundlich,[20] who investigated the Tyndall light of flowing iron-oxide sol. The Tyndall light is also markedly influenced by the shape of the colloidal particles.

In sufficiently old and concentrated sols a constant value of double refraction is attained which is independent of the rate at which the fluid flows. It may be assumed that, in this state, practically all particles are orientated and contribute to the double refraction. If this is measured quantitatively, the double refraction of the V_2O_5, contained in the sol, may be calculated,

assuming that we have a thin lamella of the pure substance V_2O_5. This double refraction was compared with the double refraction of a thin crystal of molten V_2O_5. The values were found to be nearly the same.[21] This is due to the fact that the double refraction of the sol is merely caused by the double refraction of small V_2O_5 crystals and the so-called rod-like double refraction is negligible. This rod-like double refraction may be caused by optically isotropic particles, which are not in themselves doubly refracting, but yield doubly refracting structures, provided they have an elongated form and are regularly orientated.[22] This result would be conclusive, if we were sure that the particles in the sol have exactly the same chemical constitution as molten V_2O_5.[23]

Theoretically double refraction is correlated with *dichroism*. Many of these sols, especially the sols of V_2O_5, iron oxide and also sols of dyestuffs, such as benzopurpurin, aniline blue, etc., not only exhibit a strong double refraction but also a pronounced dichroism provided the particles are orientated in a regular way. Polarized light passing through lamellæ of a flowing sol of this kind has a colour which depends upon the angle between the vector of the illuminating beam and the direction of flow. Double refraction and dichroism are correlated by a rule which is claimed by Zocher [24] to have a very general bearing. For the sake of simplicity it is assumed that the dichroism is so pronounced that the so-called extraordinary ray is not appreciably absorbed, while the ordinary ray is strongly absorbed. I may add that the extraordinary

ray has a vector parallel to the axis of the particles, the ordinary ray a vector perpendicular to it. This leads to a negative dichroism. Let us assume further that the absorption lies in the green portion of the spectrum. Between the index of refraction and the wave-length of the extraordinary ray there exists the simple relation as shown by curve 1 in the following

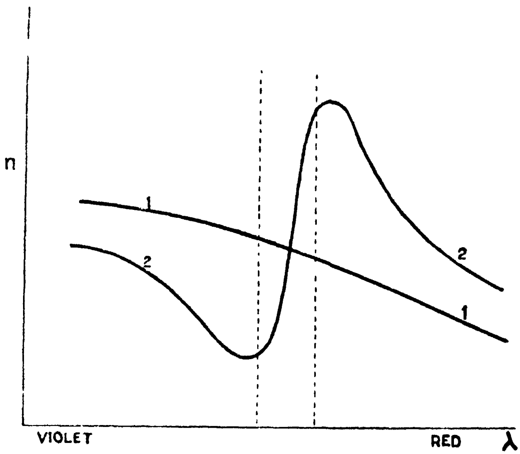

FIG. 39.

Fig. 39. The indices of refraction are plotted as ordinates and the wave-lengths as abscissæ. For the ordinary ray on the other hand we have curve 2 representing the well-known influence of absorption on dispersion. This need not be the relative position of the two curves, but it is the most probable one. Positive double refraction is observed when the index of refraction of the extraordinary ray is greater than that

of the ordinary ray, while negative double refraction is the reverse. It is evident from Fig. 39 that the double refraction in the blue and violet must be positive and negative in the red. This complicated behaviour was actually observed by Zocher[25] in the case of an aniline-blue sol, a colloidal solution with non-spherical particles. All the characteristics of the above described examples are met with in this sol. Strong absorption in the green, negative dichroism, negative double refraction in the red and positive in the blue. The relationships in the following table have been confirmed in a general way for a number of anisotropic sols.

TABLE 19

Negative Dichroism.	*Double Refraction.*
Absorption range in middle of spectrum	*Negative* in *red*, *positive* in *blue*.
Absorption range in *red* end of spectrum	*Positive* in remainder of spectrum.
Absorption range in *blue* end of spectrum	*Negative* in remainder of spectrum.
Positive Dichroism.	*Double Refraction.*
Absorption range in middle of spectrum	*Positive* in *red*, *negative* in *blue*.
Absorption range in *red* end of spectrum	*Negative* in remainder of spectrum.
Absorption range in *blue* end of spectrum	*Positive* in remainder of spectrum.

In the cases discussed so far the cause of the non-spherical shape of the particles and the double refraction and dichroism of the sols, is always the crystalline state of the colloidal particles. Cases will now be

considered in which the correlation between the shape of the particles and their optical properties on the one side, and the state of aggregation on the other is not so simple. Sols are known which show double refraction although their particles are crystals of the regular system (which do not exhibit double refraction under normal circumstances). Björnstahl [26] has found that gold and silver sols, whose particles give the normal X-ray diagram of the massive metal and have therefore crystallized in the regular system, show a quite noticeable double refraction and dichroism. Herm. Ambronn [27] noticed many years ago that crystals of gold and silver which have formed in very narrow spaces between two glass plates or in the pores of fibres, are doubly refracting and dichroic. The conditions under which the particles of these gold and silver sols are formed, seem to be such that a large proportion of them are not regular but more or less distorted. They most likely exist as lamellæ like the particles formed in narrow spaces. This distortion is the cause of the double refraction and it is not due to their natural crystalline form.

Non-spherical shape and double refraction may also be caused by the fact, that the state of the particles is not crystalline but mesomorphous. That is to say, they exist as so-called crystalline liquids. The use of a more general term "mesomorphous" seems to be very advisable. This is a state of aggregation midway between the true crystalline state and the irregularity of the amorphous state. It is a state of higher symmetry than the crystalline one. The molecules

may lie for instance symmetrically about an axis, the position of each molecule being quite accidental; or they may be piled in layers, the position of the molecules of a single layer being haphazard. This is the state of aggregation which Friedel [28] called mesomorphous and the crystal liquids belong to it. As I mentioned before, I believe that more consideration should be given than heretofore to the possibility that the particles of some sols exist in this state of aggregation. If for instance aqueous solutions of 10-bromophenanthrene-3- or 6-sulphonic acid [29] or of salvarsan [30] are carefully evaporated, very fine drops are formed which show a dark cross between crossed Nicol prisms. These droplets are a concentrated solution of water in the organic substances, which show the behaviour of liquid crystals. Since the aqueous solutions of salvarsan and of the sulphonic acids show in many respects a colloidal behaviour, it is only likely that the particles which they contain are mesomorphous. Mesomorphous particles are most likely also found in soap solutions. Under special conditions these solutions contain very long threads whose length may reach values up to 100μ while their thickness is often ultramicroscopic.[31] Now ammonium oleate was always considered to be a liquid crystal, and thread-like forms are not characteristic of crystals, but they are frequent in substances in a mesomorphous state. It seems to be very likely that these threads in soap solutions are mesomorphous.

Recently a case was found where quite different conditions caused a non-spherical shape of the particles.[32] It has been known for some time that latex, the sap of

india-rubber trees, from which india-rubber is obtained, contained particles of an extraordinary shape. The particles in the latex are not colloidal throughout, a certain fraction of them having dimensions larger than ultramicroscopic. They have a length up to 2-4μ and they therefore are visible under the microscope. Now these particles in the latex of the most important rubber tree, *Hevea brasiliensis*, are mostly pear-shaped. That the smaller particles also are not truly spherical follows from the fact that they show marked scintillations when viewed under the cardioid ultramicroscope with an azimuth diaphragm. But these particles do not look like crystals, they look like drops which would assume a spherical shape, if not prevented by a tough exterior skin. The existence of such a skin has been shown by using a so-called micromanipulator, a microdissection apparatus.[33] This instrument may be used in colloidal chemistry for many purposes. It consists of very fine glass needles, whose points are not thicker than 0·5μ. They are moved by fine screws under the microscope. If the particles of latex are embedded in a suitable gel, which prevents the latex from evaporating, they may be examined with these microdissection needles. It turned out that the interior of the particles behaved like a stiff fluid, perhaps of the consistency of honey. The exterior of the particles behaved like a harder skin. The difference between the interior of the particles and the outer skin was especially marked, if benzene was introduced into the particles by means of the micromanipulator and a micropipette. The interior of the particles became less viscous and ran

out of the skin and the skin stuck to the needle. The entire character of the skin, its refraction and its behaviour towards organic liquids show that it consists of hydrocarbons similar to the interior of the fluid. The latex of other rubber trees, for instance of *Manihot glaziovii*, contains rod-like particles, which seem to consist of an amorphous solid. Still others like that of *Ficus elastica* contain globules, which are not surrounded by a skin, but easily coalesce when they come near enough to one another. The structure of these particles seems to be important from the standpoint of the stability of the latex, and there seems to be a parallelism between this structure and the "nerve" of the india-rubber obtained from the latex. The india-rubber has more nerve when the particles are not entirely fluid, but have a solid exterior skin. If the two-phase system of the latex persists in india-rubber then we arrive at a rational explanation of the Joule effect in india-rubber. It is also possible to account for the remarkable X-ray pictures obtained by Katz.[34] He found an amorphous diagram for unstretched india-rubber and a crystalline diagram for the stretched rubber. This crystalline diagram appeared superimposed upon the amorphous diagram.

Here we have an example of how the state of aggregation and the shape of particles has to be considered in a case which has not only biological but also technical interest. In biology systems of this kind are most likely very frequent. Fibres and tissues are often, perhaps generally, built up of particles which are nonspherical and mostly microcrystalline.[35] This was first

shown for the cellulose fibre of wood and cotton.[36] Elongated particles have also been detected in connective tissue by the aid of the azimuth diaphragm.[37]

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CHAPTER VII

EXTENT AND CHANGE OF SURFACE IN COLLOIDAL SYSTEMS

ONE of the greatest difficulties in colloidal chemistry arises from the fact that relative measurements are usually the only ones we are able to make. If we compare the properties of two crystals of rock salt, for instance, we find values which differ as a rule only to the extent that the instruments are incapable of exact duplication of results. Furthermore no difficulty is experienced in repeating such measurements at any time. But two sols of the same substance, prepared as nearly alike as possible by the same method, generally show much greater differences in their properties than is shown in the case of crystals. We must content ourselves with the comparison of the properties of one and the same sol. Furthermore we must bear in mind that sols generally change their properties in the course of time. They show a certain ageing and comparable results may only be obtained when the measurements are made after equal lapses of time. This behaviour is due to various causes. The sols contain foreign substances in variable amounts and these may cause a difference in behaviour of two

sols. Then too the magnitude of the particles and therefore the interface between them and the surrounding medium may be different in the two sols and it may change in the course of time. This is a further cause for the relativity of the properties of two sols and for their ageing. This behaviour holds for practically all colloidal systems as well as for gels or for dry gels like charcoal. It is therefore of the utmost importance to be able to measure the surface of a colloidal system absolutely or to follow its changes in the course of time. This chapter contains a survey of some new investigations which deal with this subject.

It is not always easy to answer the question as to the extent of the interface of a colloidal system. What, for instance, is the magnitude of interface in a colloidal solution whose particles are so small that they are not visible under the ultramicroscope and cannot be counted? What is it in the case of a substance like charcoal, which is enormously porous and whose effective interface is not defined by its outer surface, but by its so-called interior surface? Even in systems of coarser particles a measurement of their dimensions under the microscope only gives satisfactory results if the particles are of practically the same size and have a regular shape. It is therefore important that Paneth [1] succeeded in measuring the extent of such interfaces with a considerable degree of certainty in a rather independent way. He measured the interface between a liquid and powders consisting of particles of a difficultly soluble salt like lead sulphate, whose metallic constituent has an isotope. Such a salt adsorbs iso-

topes, for instance in this case it adsorbs ThB on its surface and this adsorption was determined. The theory of isotopy requires that the ratio of Pb¨-ions $Pb_s^{\cdot\cdot}$ to ThB¨-ions $ThB_s^{\cdot\cdot}$ in the solution must be the same as the ratio of the Pb–atoms Pb_0 to ThB–atoms ThB_0 on the surface of the $PbSO_4$ crystals.

$$\frac{Pb_s^{\cdot\cdot}}{ThB_s^{\cdot\cdot}} = \frac{Pb_0}{ThB_0}.$$

In this formula all quantities may be determined experimentally except Pb_0, the number of Pb-atoms on the unit of surface. Therefore Pb_0 may be calculated from this formula, if the adsorption of the ThB and the concentration of Pb-ions in solution are once measured. This value of Pb_0 evidently makes it possible to measure the magnitude of the specific surface of the crystals, that is the surface of 1 g. since the value for the surface of a single lead sulphate molecule may easily be calculated.

Paneth compared this radioactive method of measuring the specific surface with a direct method of measurement. He determined the dimensions of the crystals under the microscope, and found the two methods to be in satisfactory agreement. Furthermore he measured the adsorption of dyestuffs on the crystals whose specific surface he had determined by the radioactive method and found that the adsorption layer was practically unimolecular. It must be remarked here that the adsorption isothermal of these dyestuffs shows a state of saturation, which means that with increasing concentration a maximum amount of adsorption was

reached. This value was used for calculating the thickness of the adsorption layer.

For animal charcoal this radioactive method is not feasible. But Paneth tried to determine the specific surface of charcoal by generalizing the last-mentioned experiments and by assuming that in the case of charcoal the adsorption layer of dyestuffs, in the range of saturation, is unimolecular. It might seem rather bold to push the analogy to this extent. Paneth therefore tested his assumptions to see whether the behaviour of diamond powder towards methylene blue, in aqueous solution, agreed with the ideas advanced. The surface of the powder was determined microscopically and the adsorption measured at the state of saturation. The layer of adsorbed dyestuff was found to be practically unimolecular. Making the same assumption for animal charcoal, the specific surface was found to be equal to 200 square meters. Smaller values, but of the same order of magnitude, were found for other kinds of charcoal. Similar results were obtained using other dyestuffs and also lead nitrate, a substance of quite different character.

Experiments of the same kind may be done with colloidal solutions. Their particles practically always adsorb dyestuffs, those of negative sols adsorbing basic dyestuffs, those of positive sols adsorbing acid dyestuffs more strongly. The adsorption isothermal often shows a distinct range of saturation. For instance this is the case in the adsorption of eosin by the particles of a sol of iron oxide.[2] Assuming again that the adsorption layer is unimolecular, the specific surface of these

iron-oxide particles was found to be equal to about 20 square meters.

It should be possible to follow the change in the extension of the interface of colloidal particles by making experiments of this kind after various intervals of time. This has not been done as yet. But a phenomenon is known where indeed a change of surface extent is made perceptible by a change in adsorption. This is the so-called reversal of adsorption.[3] It was found very distinctly when an Odén sulphur sol was coagulated with dyestuffs like new fuchsine. The coagulated sulphur is first separated out of the sol in the form of a coherent red clot, the fluid being practically colourless. In the course of time the clot is disintegrated, until at last a large number of microcrystalline particles are formed which are imperfectly wetted by the fluid. Running parallel to this change, the colour of the fluid again changes to a deeper red. This behaviour can be readily explained by assuming that the particles of the sulphur become larger and larger and that their interface correspondingly diminishes. Therefore a part of the adsorbed dyestuff is given back to the fluid. It has not been decided as yet whether this reversal of adsorption is due to a progress of coagulation or, what is more likely, to crystallization of the coagulated sulphur.

Up to the present the reversal of coagulation has not been found to be such a general phenomenon that it could be used to any great extent in following the changes of interface in sols or gels. A radioactive method developed by Hahn[4] has been more successful

and is rather more promising. He added a small amount of a radioactive element such as RaTh, which transformed itself into an emanation, to solutions of ferric chloride, aluminium chloride, etc., and then precipitated the hydroxide by the addition of alkali. The hydroxide adsorbs the RaTh. It is filtered off and the amount of emanation given off is measured from time to time, the hydroxide being subjected to various conditions. As long as it is kept moist, the emanation escapes to a very large extent, almost to the theoretical value. In the case of $Fe(OH)_3$ 80 per cent. and even more of the emanation escapes. If the hydroxide is dried or heated, the emanating capacity is greatly lowered.

These changes are not caused by any change in the adsorbability of the emanation. The emanation is practically not adsorbed at all by the particles of these hydroxides. The real reason is that the particles undergo changes by which the extent of their free interface is altered. As long as the particles are very small and separated from one another by films of liquid, a large part of their interface is free and the emanation is able to escape readily. This is the state of a fresh moist hydroxide. In the course of time, by drying or heating, the extension of free interface is more and more reduced, because the small primary particles are coagulated to coarser clusters or develop into larger crystals. Parallel with this reduction of free interface, the emanating capacity is lowered. Hahn found that the changes in these hydroxide gels, caused by drying, are the result of two distinct in-

fluences, a reversible one and an irreversible one. Iron hydroxide shows the reversible change. If the dried iron hydroxide which has lost its emanating capacity to a large extent is moistened again, the emanating capacity rises once more and nearly reaches the original value. Nickel hydroxide, on the other hand, when treated in like manner, shows an almost irreversible change. The emanating capacity increases very little after remoistening. This behaviour is shown by Figs. 40 for iron hydroxide and 41 for nickel hydroxide. Here the abscissæ are the time t, the ordinates the emanating capacity ϵ. The signs 0 per cent. and 90 per cent. show that the hydroxides are kept either dry or moist respectively. It is very likely that the reversible change is due to a coagulation effect, the coagulated clusters being peptized again by remoistening. The irreversible change is most likely caused by a growth of the small particles into larger crystals.

It could be shown that the larger crystals really form a gel which shows a smaller free surface and therefore a smaller emanating capacity. Hahn added RaTh to iron oxide sols of very different age, freshly prepared sol on the one hand and some ten to twenty years old sols on the other. The old sols contain much larger crystals. This was shown more especially by their stronger double refraction and dichroism. These are two properties closely related to the size of crystals in colloidal solutions, as was discussed in the last chapter. The gel coagulated by electrolytes from a twenty year old sol has an emanating capacity of only 35 per cent.

whereas the gel coagulated under similar conditions from the fresh sol has the much higher emanating capacity of about 70 per cent.

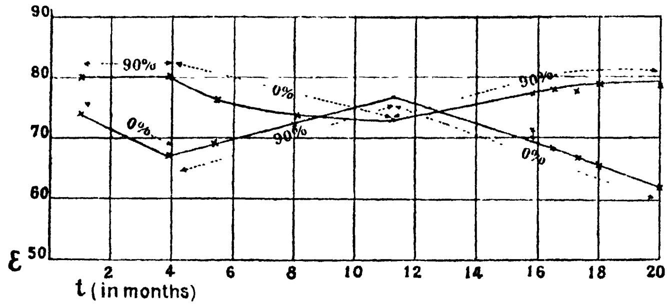

FIG. 40.

It might be expected that a hydroxide sol would be the more stable the smaller the tendency of its particles to crystallize. And this tendency would be expected to

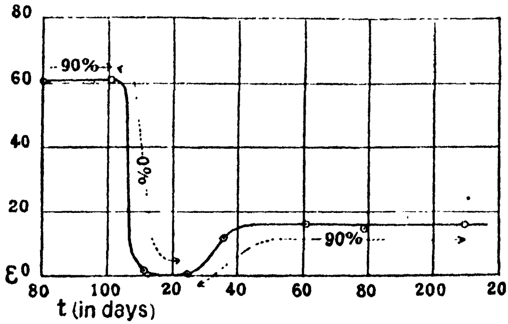

FIG. 41.

be greater the more pronounced the irreversible change becomes. This is shown by gels precipitated out of these sols and investigated by the method of Hahn.

This seems to be so since iron oxide and thorium dioxide, which exhibit only a small tendency to irreversible changes, give stable sols; on the other hand, nickel hydroxide definitely tends to show irreversible changes and gives only an unstable sol. Perhaps this method of Hahn may also be valuable in following changes which go on in other gels or gel-like colloidal systems. The changes going on in soils during drying and wetting or the hardening of portland cement could also be followed in this way.

A method of quite a different kind also leads to the conclusion that the changes which colloidal systems undergo throughout a period of time, may be caused by more than one factor. This was found, for example, in the change of double refraction in colloidal solutions of V_2O_5 and some dyestuffs like benzopurpurine. In the foregoing chapter mention was made of the fact that the double refraction of these sols is first noticeable when the particles of the sol become orientated in a regular way. This orientation can be achieved by different means, for example under the influence of a magnetic field or by letting the liquid flow in a regular manner. In the experiments discussed here, the double refraction was produced by letting the sol flow perpendicularly through a tube having a rectangular transverse section. The double refraction was measured quantitatively under comparable conditions.

As was also mentioned before, a fresh V_2O_5-sol shows practically no double refraction. In the course of time double refraction appears and this increases as the sol ages. This change is correlated with a growth of the

particles as is shown by ultramicroscopic investigation. The rate of this increase of double refraction was measured under constant conditions of experiment. It was found that the rate was influenced very largely by the presence of small amounts of foreign substances.[5] Substances of this kind may be contained in the NH_4VO_3, which is used to prepare the sol. This is the reason why the increase in double refraction for

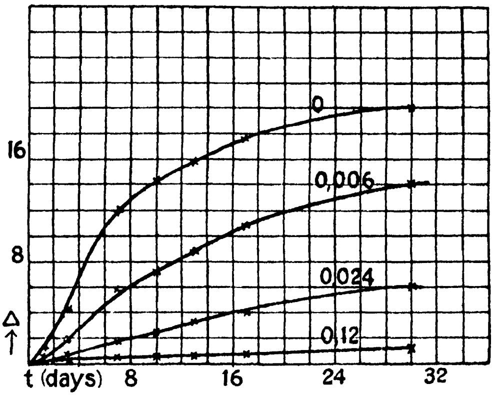

FIG. 42.

different sols proceeds with such very different velocities. Arsenic acid was found to be a very active substance. Very small amounts of it are able to retard the rate of change. In Fig. 42 the abscissæ represent the time t, the ordinates the double refraction Δ. The different curves refer to different concentrations of As_2O_5, the numbers being millimoles per liter of this substance.

This retarding influence is not to be explained, if one

assumes that the changes, with time, going on in the V_2O_5-sol are caused by a coagulation of its particles. As_2O_5 does not influence the coagulation of V_2O_5-sol by electrolytes in any way. It must therefore be assumed that the change is due to a crystallization of the V_2O_5-particles. The smallest particles dissolve and the larger ones grow.

This process might be influenced by the As_2O_5 provided the latter substance is adsorbed on the surface of the V_2O_5-particles and as a result lowers the rate of crystallization. It is well known that impurities adsorbed on the surface of crystals may retard their velocity of crystallization. The manner in which the rate of change depends on the concentration of the As_2O_5 agrees well with this assumption.

Here we have a case where the ageing of a sol, made visible by its change in double refraction, is caused by a crystallization of the colloidal particles. But there are certainly other cases where a change in double refraction is produced by a coagulation of the colloidal particles. If solutions of benzopurpurine are prepared by heating benzopurpurine, free from electrolytes, with water, the solution is not doubly refracting provided it is sufficiently dilute. The sol does not change its behaviour even over a period of many months. But if a small amount of electrolytes be added the sol quickly becomes doubly refracting. The behaviour of different electrolytes shows that in this case we are dealing with a phenomenon of coagulation.[6] Since the particles of the benzopurpurine sol are negative, the cations are of greatest influence and their influence

depends on their adsorbability and valency. A bivalent cation requires a much smaller concentration, in order to produce a certain double refraction in a given time, than does the univalent cation. Other phenomena correlated with coagulation are also found here, for instance the protective influence of hydrophilic colloids such as gelatine.

If this change in double refraction after the addition of electrolytes is followed quantitatively, the rate of change differs distinctly from that measured in the case of the V_2O_5-sol.[7] At first there is a rapid change which is followed by a more gradual one. The first rapid growth is most likely caused by coagulation. The gradual change which occurs later is perhaps due to a similar kind of crystallization as in the case of the V_2O_5-sol. But other facts seem to show that we are dealing with a coagulation of coarser particles.

In the benzopurpurine sol the changes are also more reversible than in the V_2O_5-sol. The double refraction disappears when the sol is heated and this phenomenon follows the rules for the peptization of colloidal solutions. For instance, the temperature which is necessary to cause the disappearance of the double refraction is lower if the cation producing the double refraction has only a weak power of coagulation.[6]

It may be added that this coagulation is somewhat different from normal coagulation, in so far as it causes the formation of regularly orientated clusters of particles and not irregular clusters. We have an orientated coagulation which has to be distinguished from the normal irregular coagulation. Such an orientated co-

agulation only proceeds as long as the concentration of electrolyte is sufficiently small. At high concentrations the irregular coagulation preponderates. We have again a competition between the grouping velocity and the orientating velocity, which was discussed in the foregoing chapter (see p. 94). This competition is also shown by the following experiment.[8] It has been mentioned that double refraction is produced in a benzopurpurine sol provided a small amount of electrolyte is added. We have under these circumstances an orientated coagulation giving regular orientated clusters. If on the other hand a large amount of electrolyte is added, the benzopurpurine is precipitated out of the solution. The clusters coagulated rapidly in this way are irregular. When they are peptized in water, a benzopurpurine sol is formed which shows no double refraction.

Just as in the cases investigated by Hahn we have here two influences changing the distribution and magnitude of the particles in colloidal systems, a coagulation which is more reversible in the case of the benzopurpurine sol and a crystallization in the case of the V_2O_5-sol.

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CHAPTER VIII

PHOTODICHROISM AND SIMILAR PHENOMENA

THE foregoing chapters have already shown how studies of double refraction and dichroism may give us important clues to the structure of colloidal systems. In these cases the orientating influences causing the anisotropy were the movement of the liquid and the magnetic or electric fields. It is very remarkable that there are other colloidal systems in which light is able to cause double refraction and dichroism. Systems of this kind are the so-called photohaloids which were first named and investigated thoroughly by Carey Lea.[1]

The photohaloids belong to a class of colloidal systems which may be called solid sols. For instance the dispersion medium may consist of silver chloride, in which silver is present as the disperse phase. Such photohaloids are the coloured substances which are formed when light darkens a silver haloid. But Carey Lea and others were able to show that they may be formed under quite different conditions, for instance by coagulation of a mixture of a silver sol and a silver haloid sol. They belong to a larger group of colloidal

systems, which are characterized by the fact that the metal of a metal salt is dispersed in the salt itself. R. Lorenz [2] has investigated systems of this kind, especially the so-called pyrosols of lead dispersed in melted $PbCl_2$. If this sol is cooled and made to crystallize, a solid sol is formed similar to the photohaloids.

Remarkable photochemical properties of the photohaloids, especially of the photochlorides, have been known for some time. The photochloride is able to assume to a certain degree the colour of the light with which it has been illuminated.[3] If a spectrum is projected on a layer of photochloride, it is photographed in its true colours, the red and the blue being very pronounced. Weigert [4] has shown furthermore that light was able, not only to imprint its colour on the photochloride, but also its direction of polarization. He used for these experiments glass plates which had been covered with a thin layer of an emulsion of silver chloride in gelatine. It was dried and then illuminated with light until the colour of the emulsion turned to a bluish-red. If such a plate is then illuminated with polarized red light, a red spot is produced which shows dichroism and double refraction. The dichroism is visible if one looks at the spot through a Nicol. The spot looks brightest if the vector of the light passing through the Nicol has the same direction as the vector of the light which had caused the spot. It looks darkest in a direction perpendicular to this. Fig. 43 shows this effect objectively. The spot 1 was caused half by horizontally and half by vertically polarized light, spot 2 by vertically polarized light, and spot 3 by

Fig. 43.

horizontally polarized light. These spots were copied on a photographic plate using in the first row natural light, in the second row vertically, and in the third row horizontally polarized light. It is easy to see that the spots are brightest when the directions of polarization are identical.

The double refraction becomes visible if the spot is placed between crossed Nicols.

Weigert showed that this *photodichroism*, as it may be called, is not confined to the photochlorides. He found that quite a number of dyestuffs, such as malachite green, fuchsine, methylene blue, pinachrome, and others show this effect when dispersed in a collodion gel. They give it in a remarkable form, especially in low concentrations.

The following statements will always refer to the photochloride if no mention is made to the contrary. We are dealing with very diverse phenomena. The light used for causing the spots may be called the exciting light. If its colour is changed, it is found that light of all colours has a photodichroic effect. It is strongest for red light and very weak for violet light. Then too the photodichroism of the spot is different for different colours of the spectrum, and it changes greatly with the length of time used for generating the spots. In the accompanying three figures, 44-46, the time of excitation t is plotted as abscissæ, the photodichroism Φ as ordinates. Fig. 44 refers to an excitation with red light, Fig. 45 to one with green light, Fig. 46 to one with blue light. The photodichroism is counted positive if it behaves as mentioned above.

In that case the spot is brighter when the light, passing through the Nicol, has the same direction as the vector of the exciting light. The photodichroism is counted negative when the behaviour is just the opposite. The figures show that at the beginning the photodichroism is practically always positive for the light which is

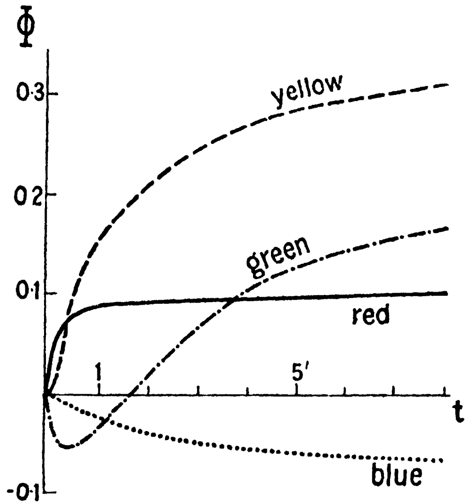

FIG. 44.

identical with the exciting light. For the other colours the photodichroism is generally negative at first.[5] The gels containing dyestuffs, which were mentioned above, also show this behaviour towards light of various colours.

Weigert found a similarly complicated behaviour for the *photo double refraction* of these photochlorides, for

light of different colours, and when the duration of excitation varied.

It is no easy task to explain this behaviour of photodichroism and photo double refraction. Weigert gave an explanation assuming that the particles of silver are dispersed in the silver chloride with variable density of packing. He assumed further that the different

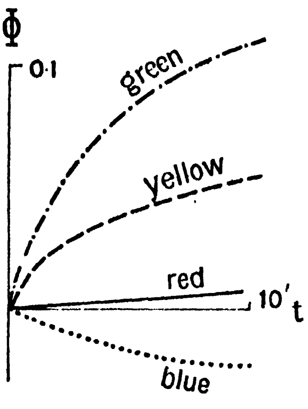

FIG. 45.

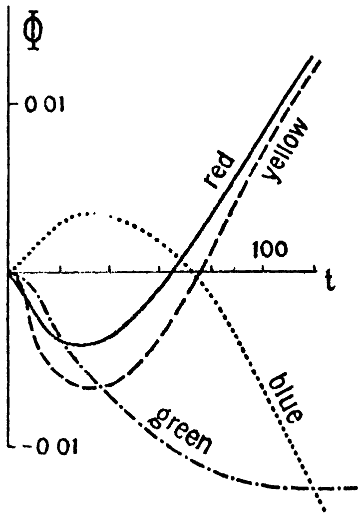

FIG. 46.

clusters thus formed show a different absorption for light of different colours, and that they are changed under the influence of polarized light in respect of their density of packing. He therefore arrived at a possible explanation for the photodichroism which was excited by light of different colours.

Another explanation, given by Zocher,[6] is perhaps

just as plausible, and it connects these phenomena of photodichroism with phenomena of a different kind. Zocher found that thin transparent mirrors of silver on glass plates could be made dichroic by polishing. This dichroism changes with the colour of the light. It is usually positive for red light and it diminishes with shortening wave-length, becoming negative for

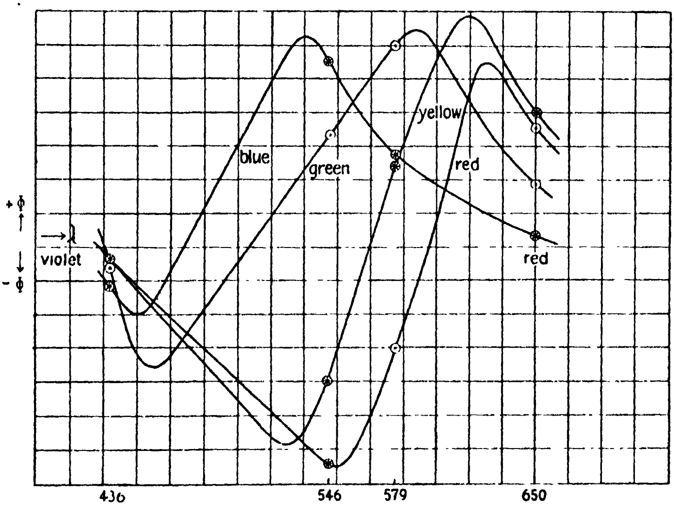

FIG. 47.

blue light. The dichroism of these silver mirrors also depends on the magnitude of their particles. The mirrors were prepared by drying sols having particles of different magnitude. Table 20 and Fig. 47 show the extent of the connexion between the dichroism of the polished silver mirrors and the photodichroism of the photochloride layer. Table 20 reproduces the dependence of the dichroism of the polished silver

mirrors on the wave-length and on the magnitude of the particles. The colour of the transmitted light gives a clue to the size of the particles ; the reddish-brown mirrors have the smallest, and the green the largest particles.

TABLE 20

Colour of the Ag-mirror in Transmitted Light.	Dichroism for			
	Red.	Yellow.	Green.	Blue.
1. Brownish-red .	+	+	+	—
2. Violet . .	+	+	—	—
3. Blue . . .	+	—	—	—
4. Green . .	— ?	—	—	—

The zero-point of the dichroism agrees well with the maximum absorption by the mirrors. For the green mirrors with the largest particles the zero-point lies in the red, for the reddish-brown ones, with the smallest particles, it lies in the blue. Fig. 47 gives the dependence of the photodichroism Φ on the wave-length of the light and on the colour of the excitant light at brief excitation, based on Weigert's measurements. The wave-lengths are abscissæ, the photodichroism is the ordinate ; the individual curves each refer to excitation by light of a different wave-length. Even cursory inspection shows a similarity to the behaviour of the dichroism in Table 20. Excitation by means of red light leads for the majority of particles to a negative photodichroism, and for the red-absorbing particles of the green silver mirrors the dichroism is also negative

(see Table 20). Excitation with blue light results principally in positive photodichroism, and the same applies to the dichroism in the case of the blue-absorbing particles of the reddish-brown silver mirrors. It seems correct to correlate these phenomena with the phenomena of photodichroism, because the particles of silver are not only made dichroic by polishing, but also may be formed in a dichroic state from the outset, when they arise in gels, as was mentioned above (see p. 108).

It might be premature to attempt a detailed explanation now. At present we know too little concerning the manner in which light is able to change silver particles. But it seems likely that those particles of silver in the silver chloride which absorb the light most strongly, would be excited most. In the case of excitation by red light, these would be the largest particles. The photodichroism caused by the red light might therefore be expected to be similar to the dichroism caused by polishing a mirror with large particles. It would be positive for red light, negative for all other colours. This is indeed the case, as is shown by Fig. 47, for a short excitation by red light. Similar considerations hold for excitation by light of another colour. If the excitation lasts a longer time, the weaker absorption of all the other particles of silver comes into play and this may cause those changes of photodichroism, in the course of time, as shown by Figs. 44-46.

The complicated correlation as mentioned between dichroism and double refraction (p. 105) seems to hold

in this case also. As a result we find the changes of photo double refraction in course of time and for an excitation with light of different colour which were mentioned before.

The influence of circularly polarized light on photochlorides is very remarkable. Here we find two phenomena corresponding to double refraction and dichroism. The phenomenon corresponding to double refraction is the *rotation of the plane of polarization.* This rotation is explained by the assumption that there are two waves of circularly polarized light which pass through the medium with opposite rotation. If the one wave is retarded as compared with the other, the plane of polarized vibration is rotated. Therefore the rotation of the plane of polarization is caused by a difference of phase between two circularly polarized waves of the opposite sense of rotation, just as ellipticity in the case of normal double refraction is caused by a difference of phase between two plane polarized waves. The phenomenon corresponding to dichroism is the unequal absorption of the two circular components. It is called *circular dichroism* and was first investigated by Cotton.[7]

The photochloride films, used by Weigert, are not suitable for the investigation of any possible influence of circularly polarized light which is comparable to the influence of plane polarized light causing photodichroism, for the gelatine, contained in these films, produces a rotation of the plane of polarization itself. But Weigert [8] had shown already that a photochloride film, containing no gelatine, shows photodichroism,

and Zocher and Coper [9] have extended these investigations. They used silver mirrors precipitated from an ammoniacal solution of silver tartrate, on thin glass plates. These were treated with chlorine and then converted into a film of photochloride by exposing them to light until they assumed a light red colour. Circularly polarized light was produced by allowing plane polarized light to pass through a $\frac{\lambda}{4}$-plate or a Fresnel rhomb. If the photochloride film was illuminated by such light, the spot produced by it was able to rotate the plane of polarization and it also showed circular dichroism.

It may be noted that a rotation of the plane of polarization is also produced by normal dichroism. But this effect changes in magnitude, provided the spot is turned round an axis passing through its centre. On the other hand, a true rotatory polarization remains unchanged when the spot on the photochloride film is turned round such an axis. The latter was found to be the case in the above experiments, which showed that we are dealing with true rotatory polarization.

This is the first case on record where an optically active substance is formed by a purely physical agent, namely, by circularly polarized light.

The results, discussed so far, are the more interesting because they make possible important applications to biological questions. The results of quite a number of remarkable experiments have been published which seem to show that polarized light may influence biological processes in a way quite different from ordinary

light. According to Morrison[10] colonies of *Photobacterium phosphorescens* show a stronger light when growing under polarized light compared with growth under ordinary light of the same strength. Similar experiments with other bacteria have been published by Macht.[11] These phenomena may well be caused by effects which are similar to the effects found by Weigert in colloidal systems.

Weigert[12] further pointed out that there seems to be a marked correlation between the photodichroism of the above-mentioned dilute solutions of dyestuffs in collodion gels and the behaviour of the retina. The principal fact, which he noted, was that concentrated solutions of these dyestuffs in collodion gels practically only show photodichroism for the light which they absorb strongly, whereas the dilute gels show photodichroism for all colours. These dilute gels are colour-sensitive, so to say, whereas the concentrated ones are not. Now this happens to be the difference between the two sensitive organs in the retina, the cones and the rods. The cones are sensitive to light of different colours. They are the organs of colour-vision, whereas the rods only allow a distinction between light and dark. Now the cones contain no dyestuff in any measurable amount, the rods on the other hand contain a dyestuff, the so-called visual purple. Weigert also assumes that the cones contain this dyestuff (or another one) but in so small amount that it has not been found as yet. The cones therefore correspond to the collodion gels, containing a dilute solution of the dyestuff, which are sensitive to light of

different colours. The rods on the other hand correspond to the collodion gels, containing a concentrated solution of the dyestuff, which do not allow any colour differentiation. Weigert remarks that the change of photodichroism, with the time of excitation, has a distinct similarity to the impressions left on the retina caused by intensely coloured light. Whether his theory holds or not, it is important, in any case, that we know of colloidal systems which are very weakly coloured and yet are sensitive to light of different colours, just as the cones of the retina are, The faculty of colour differentiation is not therefore. of necessity, correlated with a system containing particles of very different colours.

The production of an optically active substance by a physical agent, such as circularly polarized light, is also of biological importance. It is a well-known and remarkable fact that the optical activity of substances contained in the organized world is asymmetrical. The many optically active substances found in plants and animals are nearly always of one kind. When we find the dextro-rotary substance we do not have the lævo-rotary one. One method that is often used to obtain an optically active substance is to grow bacteria or moulds on racemic substances. The explanation of this asymmetry has always been a most difficult question. Byk [13] discussed it at length and came to the conclusion that it might be explained, provided the production of an optically active substance by a purely physical agent was known. Primitive organisms, once made asymmetrical through such an influence, might

have caused the whole organic world to become asymmetrical. He pointed out that there seems to be a certain asymmetry of the optical conditions on the surface of the earth. The polarized light of the sky is polarized elliptically by reflection on surfaces of water, for instance, and this reflected light therefore contains a certain amount of circularly polarized light. Under the influence of the magnetic field of the earth, a certain surplus of circularly polarized light of one sense of rotation would be produced. Since Zocher and Coper found a case where circularly polarized light causes optical activity, the possibility of such an effect, causing the optical activity of the organisms, cannot be denied. The objection might be raised that this optical asymmetry on the surface of the earth is not sufficiently pronounced. A further possibility of optical asymmetry on the surface of the earth was discussed by Zocher and Coper, and is connected with the magnetic rotation in substances such as liquid oxygen and solutions of some salts of the rare earths. But it seems open to a similar objection. Nevertheless the important fact remains that optical activity may really be produced in colloidal systems by a purely physical agent.

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